

Uranium recovery from phosphate rocks/minerals – A comprehensive review

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ABSTRACT

Although the use of nuclear energy is still viewed with caution due to various problems associated, such as the safe operation of 'aging' nuclear plants and the final disposal of nuclear waste, many countries in Europe are now increasingly considering nuclear energy as an alternative to reducing fossil fuel energy production. At the present stage primary sources of uranium are sufficient to meet uranium needs and secondary sources are becoming increasingly important in terms of their long-term availability and environmental friendliness. Mining/recovery of uranium from secondary sources (such as phosphate minerals) is considerably safer in terms of exposure to radiological radiation and therefore requires less stringent safety measures. Uranium is also present in waste produced from certain industrial processes such as fertilizer production industry (e.g. phosphogypsum) and in nuclear waste. This work refers to the extraction and recovery of uranium from phosphate rocks, which is directly related to the production of uranium-free phosphate fertilizers and aims to limit environmental pollution related to the use of phosphate fertilizers. Since the chemistry during the leaching step is critical to efficient uranium recovery, various investigations have been carried to study various parameters that play an important role in achieving an optimum uranium extraction from rocks. Uranium leaching is carried out under acidic or alkaline conditions and the choice of chemistry is determined by the mineralogy of the host rocks. Acid leaching yields a higher recovery than alkaline leaching because the matrix is often more resistant to alkali than to acid leaching. However, the alkaline leaching process has the advantage of leading to the precipitation of a comparatively purer product directly from the leaching liquid. In addition, the washing solutions can be regenerated for further use, making this method more environmentally friendly. Recently alternative methods have been proposed which make use of uranium complexing ligands (e.g. EDTA) to achieve more efficient and selective uranium recovery.

1. Uranium

Uranium belongs to the actinide family and natural uranium consists of three isotopes, U-238, U-234 and U-235, which are radioactive and decay by emission of mainly alpha α -particles, while the emission of β - and γ -particles is very low [1,2]. The average U content of the Earth's crust is ~ 2.8 ppm U (granite 3–5 ppm, sedimentary rocks 2–3 ppm) and in seawater it is ~ 0.003 ppm. Uranium occurs in different oxidation states: U(IV) (tetravalent), U(VI) (hexavalent) and U(III) (trivalent). The most stable oxidation states of uranium in aqueous environment are +IV and +VI [1,3]. U(VI) is the most stable oxidation state under oxidizing conditions, while U(IV) prevails in a reducing environment, forming the very insoluble UO_2 solid phase [1,4]. Uranium in the U(VI) oxidation state is relatively soluble, and its solubility in aqueous systems is mainly

controlled by three factors: redox potential, pH, and complexing agents (e.g., carbonates) [1].

Hexavalent uranium is significantly more soluble than U(IV) and is particularly stable as the uranyl ion (UO_2^{2+}) under oxidizing conditions and forms a range of mononuclear and polynuclear hydrolysis species [5]. With increasing carbonate concentrations, mononuclear uranyl carbonate species become increasingly important [6]. While the majority of carbonates are insoluble in water, uranium carbonate complexes are very soluble in aqueous solutions. This occurs because a U(VI) cation can bind up to three carbonate ligands to form anionic complexes [7]. The most abundant soluble uranium species in groundwater are uranyl carbonate complexes [8]. Uranium species distribution diagrams in the absence of carbonate (Fig. 1a) show that when the pH of a U(VI) solution is increased, uranium is converted into hydrated uranium oxide

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hydroxide ($\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$) and at high pH is transformed into an anionic hydroxide complex ($\text{UO}_2(\text{OH})_3^-$). When carbonate is added U (VI) forms a series of carbonate complexes under alkaline conditions (Fig. 1b) [9]. On the other hand, in phosphate solutions/systems it seems that basic U(VI)-phosphate complexes are the predominant species (Fig. 2) [10]. In particular, $\text{UO}_2(\text{H}_2\text{PO}_4)_2$ and UO_2HPO_4 are the major species in the acidic pH range ($\text{pH} < 5$), which is typical for acidic phosphate solutions. The formation of uranium phosphate complexes is favored due to the relatively high concentration of phosphate ions in those systems [8,11].

2. Uranium for Nuclear Energy

Due to the increasing demand for energy, the reduced availability of resources and global warming, the need to find alternative energy sources that are environmentally friendly and free from carbon dioxide emissions is imperative [12,13]. Uranium is a key element in nuclear power production, with a constantly increasing global demand [14]. For 60 years, nuclear power has contributed to meeting energy needs worldwide [15]. About 10% of the world's electricity is produced from uranium in nuclear reactors. Belgium, Bulgaria, Czech Republic, Finland, France, Hungary, Slovakia, Slovenia, Sweden, Switzerland and Ukraine get 30% or more of their electricity from nuclear reactors [16]. USA operates about 100 reactors, providing 20% of its electricity, while France generates over 70% of its electricity from uranium [17]. In addition, specialized nuclear reactors are employed to produce a wide range of radioactive elements (radioisotopes) at relatively low cost. The use of artificial radioisotopes has been widespread since the early 1950s, and there are now about 220 research reactors in 56 countries producing radioisotopes for medical and various industrial applications [18]. These nuclear power plants function mainly as neutron sources and not for power generation.

Nuclear power plants and power plants of similar power have many common characteristics. Both require heat to produce steam to drive turbines and generators. In a nuclear power plant, however, the splitting of uranium atoms replaces the burning of coal or natural gas, and the heat produced by the decomposition of U-235 nuclei is then used to produce steam that spins turbines to drive generators, producing electricity [19,20]. Although the use of nuclear energy still has some aspects that cause concern such as safety and waste disposal, many countries in Europe are now increasingly considering nuclear energy as an alternative to replace fossil fuels [21]. Many nuclear reactors in Europe will soon reach the end of their life cycle, so a decision must be made whether to maintain, increase or decrease nuclear power generation. It

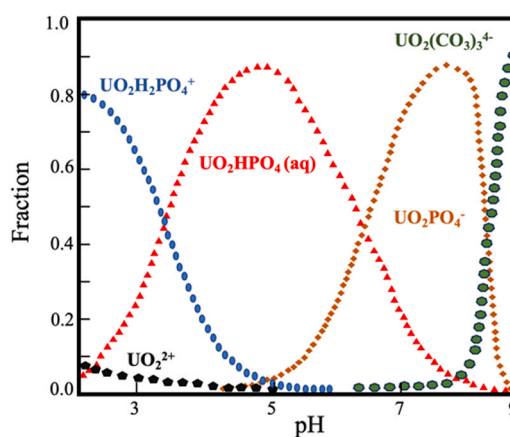


Fig. 2. : Uranium species diagram in phosphate solution ($[\text{PO}_4^{3-}]_0 = 1 \text{ mmol/L}$ and $[\text{U(VI)}]_0 = 42 \text{ } \mu\text{mol/L}$, ambient conditions) [10].

is therefore important to assess the sustainability of nuclear power in Europe. An understanding of uranium flows is essential to such an assessment, as it creates an understanding of material requirements and sources, dependencies, waste generation, accumulation, and the ability to recycle [13].

3. Effects on the environment

Wastes containing significant amounts of uranium have been produced for many years as a result of uranium mining, from uranium processing industries, nuclear power plants and research centers [14, 22]. Nuclear energy is one of the most important energy sources from the economy, safety and cleanliness point of view [23]. However, the main obstacle to the use of nuclear energy is a possible radioactive pollution with serious effects on the environment and human health. Uranium is the key raw material in the nuclear industry and is a significant pollutant due to its long lifetime, chemical toxicity and radioactivity. Long-term exposure and bioaccumulation of uranium can cause irreversible damage to the organism, cancer, muscle cramps, liver damage and nephritis [24]. Uranium is released into the environment in its hexavalent form, mainly as the uranyl ion (UO_2^{2+}), constituting a serious ecological problem and a threat to human health [25]. In addition to the uranium waste produced during the nuclear power generation process, the process of mining and processing the ore causes many

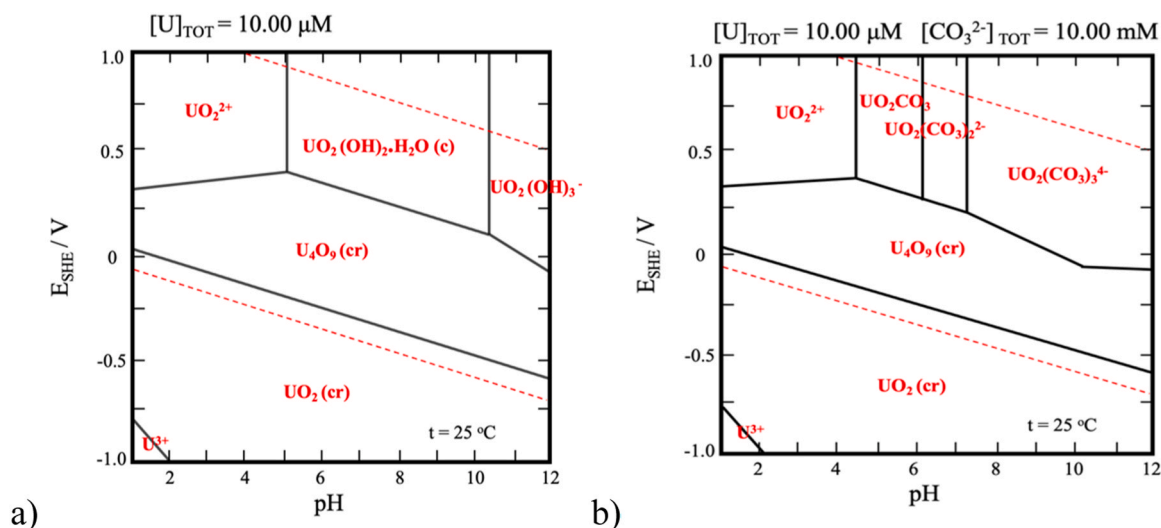


Fig. 1. E_{SHE} -pH -pH diagram of uranium species in (a) aqueous and (b) carbonate solution [9].

serious problems to the ecosystem and humans due to the contamination of water and air with dangerous radioactive substances. Uranium-contaminated groundwater and soil pose a major challenge for remediation. Many processes have been proposed for the removal of uranium from industrial liquid wastes, such as chemical precipitation, ion exchange, solvent extraction, and adsorption [14].

Nowadays, every industrial activity should be compatible with the environment and sustainable development to cover existing needs without exposing future generations to potential environmental risks and lack of raw materials. Uranium extraction should not be based solely on economic gain, but good mining and mineral resource processing guidelines should aim for minimal environmental impact, protection of human health, holistic resource utilization and zero-waste mining [26]. Uranium mining from phosphorite could become an environmentally and socially more acceptable form of uranium mining, since phosphorite is mined for phosphates anyway. Thus, the extraction of uranium from already mined phosphorites, as schematically described in Fig. 3, would lead to cleaner fertilizers with a much-reduced uranium content and to a more environmentally friendly nuclear power with its fuel obtained from sources with reduced environmental impact [26,27]. Without recovery of uranium (as well as other related resources such as rare earths) from phosphorite during fertilizer production, these resources are lost uncontrollably with the fertilizer. Such a loss of resources is potentially even more harmful to the environment, as uranium in fertilizers can affect the environment and human health [27].

3.1. Phosphate Mineral

Phosphate rocks are a source of phosphorus, which is one of the main raw materials used in the production of fertilizers and is also finds application in food supplements, beverages, and other industrial products. Phosphate resources can be classified into two categories: igneous phosphate rocks (13%) and sedimentary phosphate rocks (87%) [12]. Uranium is known to have a high affinity for phosphates and therefore occurs in all types of phosphate rocks with different concentrations [28, 29].

Phosphorite (PR) which is found in the earth's crust contains relatively high levels of environmentally toxic elements as well as valuable elements that have different applications in green and sustainable energy production [30]. Uranium is one of them and is found in PR usually at levels between 50 and 200 ppm, but some deposits contain significantly higher levels of uranium (> 800 ppm) [31]. Despite its low concentration in phosphate minerals, its recovery is important in terms of environmental and economic issues. Along with minimizing environmental impacts and protecting human health, the extraction of uranium from PR can reduce mine waste and expand its extraction resources [32].

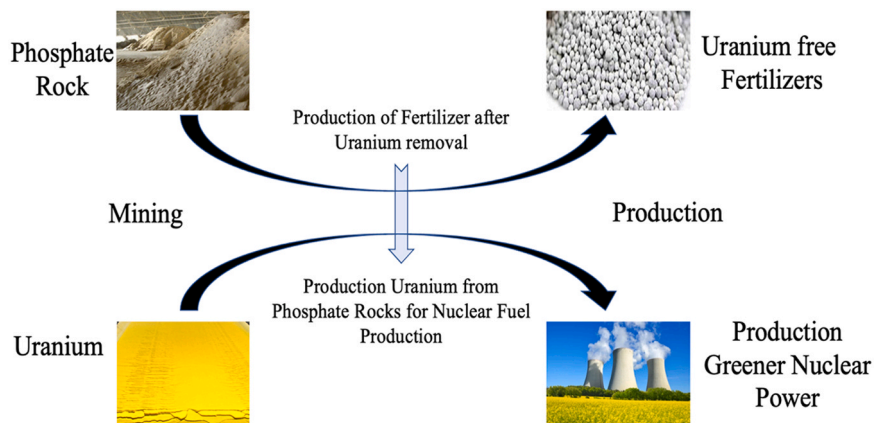
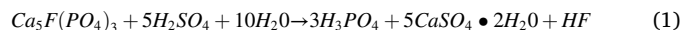


Fig. 3. : Production of phosphate fertilizers with uranium extraction leading to cleaner fertilizers and less environmental impact [27].

Recovery of U from phosphate rocks prior to fertilizer production is one measure that can be taken to produce an uranium-free product. In this way, the control of its mobility/leaching in the environment during processing can be achieved. Based on several studies, it is estimated that the amount of uranium that can be extracted during the production process of phosphate fertilizers worldwide is more than 15% of the amounts of uranium required for nuclear energy production [33].

3.2. Phosphogypsum

Phosphogypsum (PG) is a by-product produced during processing of phosphate rock to produce phosphoric acid and fertilizers [34]. About 5 tons of PG per ton of phosphoric acid are produced, while global PG production is estimated to be about 100–280 Mt per year [35]. To produce phosphoric acid, phosphate mineral is processed by either dry thermal or wet processes. The dry heat method produces phosphorus using an electric arc oven. The wet chemical phosphoric acid treatment process is widely used to produce phosphoric acid and calcium sulfate – mainly in dihydrate form ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) [36,37]. The associated equation is given in Eq. 1 and a general scheme of the processes is shown in Fig. 4.



The wet process is low cost but produces a large amount of PG, the characteristics of which are mainly determined by the composition and quality of the phosphate ore [39]. PG consists of mainly $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ but also contains impurities such as H_3PO_4 , calcium phosphates, residual acids, fluorides, sulphates, trace elements (e.g. Cr, Cu, Zn and Cd)

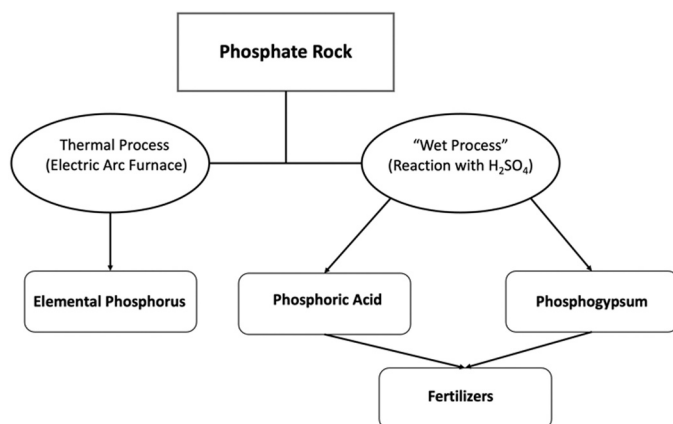


Fig. 4. : Schematic diagram of the phosphoric acid production from phosphate rocks [37].

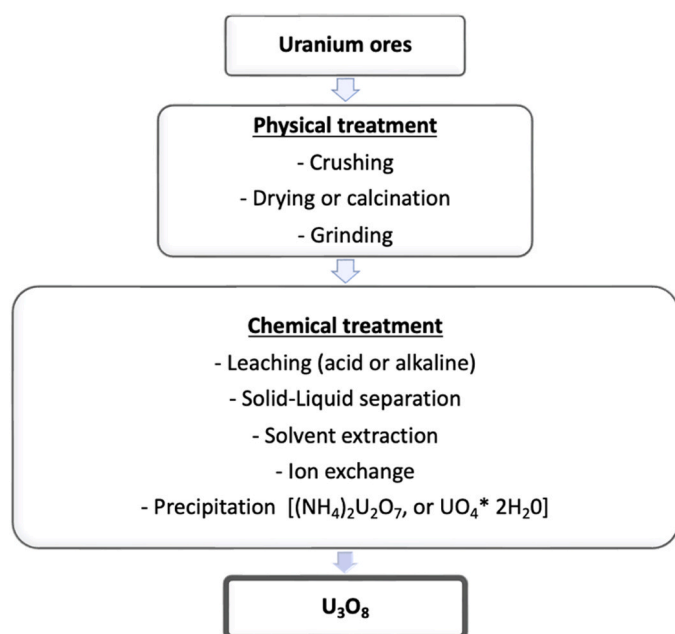


Fig. 5. : Schematic diagram of uranium recovery from rocks [38].

and even organic compounds adsorbed on the surface of the gypsum crystals [36,37]. Among other toxic elements (e.g. fluoride, heavy metals), phosphogypsum contains some natural radionuclides in relatively high concentrations. These radionuclides are members of the radioactive decay series of uranium and thorium and can cause environmental problems if disposed of without taking appropriate measures, especially when phosphogypsum with increased (radio)toxic content is used in agriculture or in the construction industry [40]. PG management is one of the most serious problems facing the phosphate industry today. Only 15% of global production is recycled, while 85% is stored near factories in coastal areas. Storage of PG without prior treatment requires large land areas and may cause serious environmental pollution of soils, water and atmosphere [37]. Furthermore, PG disposed in the environment may release radionuclides and toxic metals, which can accumulate in air, soils, and waters. Following, the pollutants may enter the biosphere causing harmful effects to living organisms, including humans [41–43].

4. Uranium recovery from phosphate rocks

Uranium occurs in nature mainly in the form of oxides. Although it forms many oxides, only two are important, UO_2 and U_3O_8 , which make up the major content of uranium ores [44]. In addition, coffinite ($\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$) and brannerite (UTi_2O_6) are the other uranium bearing minerals of significant economic importance. In following chapters studies on the extraction of uranium from rocks are presented and discussed.

The recovery of uranium from its minerals is a process that consists of multi-steps such as: crushing, dissolution or leaching, solid-liquid extraction of the leach liquor, purification of the leach slurry and precipitation of dissolved uranium in the form of yellow precipitate (yellow cake) [45]. The chemistry followed during the leaching stage is the most important factor in the process. Uranium leaching is carried out under acidic or alkaline conditions and the choice of chemistry is determined by the mineralogy of the parent rocks [46]. An oxidizer such as sulfuric acid is used for processing uranium ores containing uranite, or pitchblende, because it is more effective with most ores and does not require crushing the ore as much as the carbonate leaching process does require. Thus, the acid also breaks down other minerals found with the uranite [47].

If the minerals in the ore are over 7–8% per weight, such as those associated with high calcium content, alkaline treatment is preferred because alkaline leaching is very selective for uranium and therefore the leach solutions are relatively clean [48]. Conventionally, purification of uranium loaded leachate is accomplished using an ion exchange process. This increases the uranium content in the eluting leachate which ultimately leads to a better-quality sediment in the product recovery stage. It is interesting to note that while solvent extraction is a part of the uranium separation after acidic treatment, this is not the case in alkaline treatment [49]. This is mainly due to the formation of a third phase during solvent extraction under alkaline conditions. Sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$), ammonium diuranate $(\text{NH}_4)_2\text{U}_2\text{O}_7$ and uranyl peroxide ($\text{UO}_4 \cdot n\text{H}_2\text{O}$) are the various forms of yellow precipitate products produced during alkali treatment. The rate of dissolution of uranite is slower in alkaline than in an acidic system and generally the dissolution rate increases when the ores are fine-grained. The leaching process depends on a number of parameters, and these include acid concentration, degree of oxidation, leaching temperature, particle size and degree of release [24,38,50]. Table 2 summarizes the studies performed regarding uranium recovery from phosphate rocks and minerals.

4.1. Acidic extraction

The most widely used processes for the recovery of uranium from ores involves treatment of a finely ground ore slurry with sulfuric acid at high temperatures, usually in the presence of an oxidizer. Acid leaching yields a higher recovery than alkaline leaching because the host matrix is often more resistant to alkaline than to acid leaching [58]. A requirement to apply acid leaching is that the ore must contain low amounts of acid consuming components, such as lime in the host matrix [59]. The acid leaching process has the advantage of requiring a comparatively coarsely ground sample, mild reagent concentration, shorter leaching times and relatively low temperatures [60]. Acid-leached uranium-bearing solutions are suitable for subsequent ion-exchange treatment and solvent extraction.

Acid leaching applied to uranium dissolves except of uranium many other components present in the ore. Efficient separation of uranium from most impurities can be achieved by exploiting the fact that the uranyl ion forms stable complexes with compounds such as sulfates, carbonates, and nitrates [61]. If the uranium minerals contain U(IV), an oxidizing agent is added during the leaching procedure. Even if the ore does not contain U(IV), reducing species such as metallic iron that comes from the mining, crushing, and grinding steps may reduce U(VI) to U(IV) and cause problems [24]. Following the different studies/ approaches related to acid extraction are briefly presented and discussed.

Elshafea et al. (2013) conducted a study regarding the leaching of uranium from phosphate mineral using sulfuric acid in the presence of potassium chlorate as an oxidant, after previously crushing and grinding the phosphate mineral sample, to a size suitable for leaching [25]. The uranium from the milled ore was washed with 98% H_2SO_4 and potassium chlorate was added as an oxidant. The resulting liquid (green phosphoric acid solution) was separated by decantation followed by

Table 1

Major chemical composition (%) and trace element content of PG disposed on a coastal area in Cyprus [8,11].

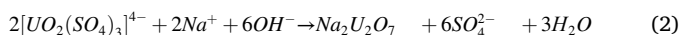
Phosphogypsum			
Major chemical composition (%)		Trace element content (ppm)	
CaO	31.0	Ba	3–100
SO_3	42.0	Zn	1–22
P_2O_5	0.02	Cl	40–125
SiO_2	0.3		
Fe_2O_3	0.05		
Al_2O_3	0.2		
H_2O (hydr.)	19		

Table 2

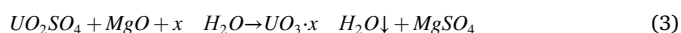
Studies carried out to achieve efficient recovery of uranium from phosphate rocks and minerals.

Extraction type	Extraction Reagents	Literature
Acidic	H ₂ SO ₄ / KClO ₃	Elshafeea et al., 2013[25]
“-”	C ₆ H ₈ O ₇ / Ca ₃ (C ₆ H ₅ O ₇) ₂	Bakry, 2021[51]
“-”	HNO ₃ / TBP	Andreou et al., 2012[34]
“-”	HNO ₃ / TBP / Na ₂ CO ₃ / NaOH	Abdelmajid et al., 2014[52]
Alkaline	(NH ₄) ₂ CO ₃ / (NH ₄)HCO ₃	Gusman et al., 1995[53]
“-”	Na ₂ CO ₃ / NaHCO ₃ / H ₂ O ₂	Shlewit et al., 2007[54]
“-”	Na ₂ CO ₃ / NaHCO ₃ / O ₂	Sreenivas et al., 2016[38]
“-”	Na ₂ CO ₃ / O ₂	Kacham et al., 2014[55]
Ligand-mediated	EDTA	Paschalidou and Pashalidis, 2019 [56]
“-”	EDTA	Paschalidou and Pashalidis, 2019 [27]
“-”	EDTA / HNO ₃	Bakry et al., 2021[29]
“-”	Resin	Al Khaledi et al., 2019[57]
“-”	D ₂ EHPA–TOPO	Hurst et al., 1972[40]
“-”	DEHCBPA	Turgis et al., 2014[44]

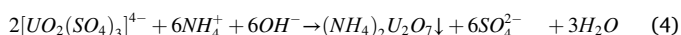
centrifugation and after dilution with deionized water. Uranium recovery from phosphoric acid was performed by solvent extraction, ion exchange and precipitation methods. The precipitation took place after the addition of 30% NaOH. The sodium diuranate (SDU) precipitated from the green solution at pH 12 (Eq. 2) was separated, washed with deionized water and dried in an oven at 105 °C.



In addition, precipitation was carried out with saturated magnesium oxide according to Eq. 3.



and by dropwise addition of 10% ammonia solution at 70 °C according to Eq. 4. At pH ~7.5 uranium is precipitated as ammonium diuranate ((NH₄)₂U₂O₇), is separated by centrifugation, washed and dried at 105 °C.



Following, the resulting yellow precipitates (Na₂U₂O₇, UO₃·xH₂O, (NH₄)₂U₂O₇) were purified by extraction with 5% tri-butyl phosphate (TBP) in kerosene, and uranium was removed from the organic phase with 0.5 M Na₂CO₃. Finally, uranium was precipitated as (NH₄)₂U₂O₇ and converted to UO₃ in a furnace at 450 °C. The uranium recovery from the ore with the use of sulfuric acid was about 48%, while Weterings and Janssen were able to recover 80% of the uranium contained in the phosphate minerals [62].

In another study, Andreou et al., presented a simple methodology, which involves acid dissolution (8 M HNO₃) of phosphogypsum, extraction with 30% tri-butyl phosphate/dodecane followed by re-extraction with deionized water (Fig. 6) [34]. The amount and/or concentration of HNO₃ is proportional to the amount of solid to achieve quantitative dissolution. It is important that the HNO₃ concentration is kept high enough to allow the formation of the UO₂(NO₃)₂·2TBP complex and the selective extraction of uranium and other actinides (eg Th (IV)) into the organic phase. Re-extraction becomes easier through the

enhanced diffusion of the NO₃⁻ anion into the pure aqueous phase, which results in the destabilization of the UO₂(NO₃)₂·2TBP complex and the diffusion of UO₂²⁺ cations into the aqueous phase. The separation efficiency of the proposed method has been estimated to be 75 ± 20%.

Abdelmajid et al. (2014), investigated the uranium recovery from phosphate ore from the Uro region in Sudan [51]. Initially, the phosphate ore samples were digested with concentrated nitric acid. The phosphoric acid was produced from the resulting powder with the aid of sulfuric acid at 80 °C.

4.2. Alkaline extraction

The alkaline leaching process has the advantage of resulting in a comparatively pure uranium product to be precipitated directly from the leaching liquor and the associated solutions are relatively non-corrosive. In addition, reagent consumption is relatively low as few ore components, except of uranium and some silicates, are dissolved by the reagent [63]. Moreover, solutions can be regenerated for further use in the washing process. However, the carbonate leaching process has also its limitations because there are uranium minerals that are not effectively degraded by carbonate leaching solutions. In addition, for the alkaline/carbonate leaching the ore must be ground finer than for acid leaching, and in some cases, increased temperature and pressure are required for enhanced uranium recovery [15].

During the carbonate leaching process (e.g. sodium carbonate or bicarbonate, ammonium carbonate) uranium is leached in solution in the form of a U(VI) carbonate complexes. The solubility of hexavalent uranium compounds in carbonate and bicarbonate media is ascribed to the formation of a stable anionic uranyl-tricarbonate complex [UO₂(CO₃)₃]⁴⁻, whose formation constant is equal to 6 × 10²². The leaching and reprocessing of carbonate ore is effective because of the strong and almost selective interaction of the carbonate anions with U (VI) compared to other metal ions present in the ore [50].

Gusman et al. (1995), recovered uranium from phosphate rocks using an alkaline/carbonate solution [53]. The associated leaching experiments showed that when sodium or potassium carbonate solutions were used, U(VI) was precipitated because hydroxide ions were generated, raising the pH of the solution. On the other hand, when ammonium carbonate/bicarbonate solutions were used, the pH did not increase due to the presence of bicarbonate ions in the solution and no U(VI) precipitation was observed. Therefore, pH buffering prevents precipitation of uranyl compounds.

To determine the sensitivity of phosphate rocks to alkaline leaching solutions for uranium extraction, leaching solution concentration, volume, and time were considered. The highest uranium extraction using ammonium carbonate/bicarbonate leaching solutions was observed at 1 M concentration, while higher concentrations did not improve the uranium extraction. The optimum leaching time was found to be 6 h, because after this time, the precipitation of ammonium diuranate started to be significant, and the amount of soluble uranium complex decreased significantly. In addition, for 10 g of concentrated phosphate rock, the maximum extraction efficiency was achieved when 50 mL of leaching solution was used. The results of this study showed that the ammonium carbonate/bicarbonate leaching process is effective in extracting approximately 40% of uranium from concentrated phosphate rock. This process is an attractive, simple, inexpensive process and ensures reduction of uranium contamination in the final product.

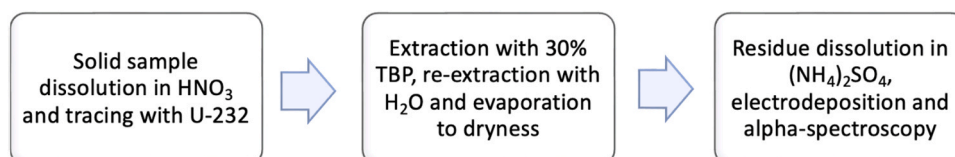
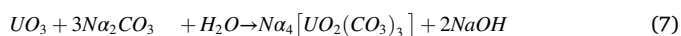
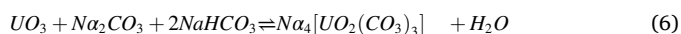


Fig. 6. Schematic diagram of uranium recovery process from carbonate rocks.

Shlewit et al. (2007), studied the recovery of uranium from phosphate minerals with carbonate solutions [54]. Phosphate samples were ground to an average particle size of 150 μm and air dried at 110 $^{\circ}\text{C}$ for 1 h. The study showed that the leaching rate of uranium increased as the concentration of sodium carbonate solution increased up to 0.5 M and then decreased when the concentration of sodium carbonate increased above 0.5 M, which may be due to the precipitation of U(VI) as $\text{UO}_2(\text{OH})_2$ hydroxide. The optimum leaching time was found to be 3 h and the recovery rate was increased with the use of hydrogen peroxide, most probably due to the oxidation of tetravalent uranium.

The reactions that describe the dissolution of uranium oxides in carbonate-bicarbonate solutions are given by (Eqs. 5–7):



In addition to its strong affinity and selectivity to uranium the carbonate leaching process has further advantages such as the production of relatively pure uranium product, that can be easily precipitated directly from the leaching liquid. Moreover, carbonate solutions are relatively non-corrosive and safer to handle than acid solutions.

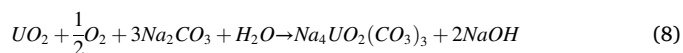
Sreenivas et al. (2015), successfully applied an alkaline process to recover uranium from carbonate rocks [38]. This process was applied on a large scale for the first time in India for the treatment of uranium minerals (Tummalapalle) and yielded a yellow precipitate with good purity (U_3O_8 77.4%) and total recovery of 65%. In addition, the process was compatible with all current terms related to technology and the environment, such as water conservation, minimal pollutants in the wastewater, etc. Moreover, the studies of Sreenivas and his co-workers have led to the development of a single process strategy for the recovery of uranium from both limestones and granites, hosted by carbonate geological bedrock, of Gogi in Karnataka. The purity of the sodium diuranate was about 82% U_3O_8 and its total recovery about 78%. The Tummalapalle mineral consumes enough acid to make alkaline treatment the only option for uranium recovery. The uranium recovery from carbonate mineral with alkaline reagents under oxidizing conditions involves the Eq. 5 (oxidation of U(IV) to U(VI) by a suitable oxidant) and Eq. 7 (dissolution of oxidized uranium with sodium carbonate/sodium bicarbonate).

During the alkaline process the dissolved uranium is generally precipitated as sodium diuranate (SDU) with the addition of a small excess of sodium hydroxide. In the alkaline process reagent regeneration is necessary mainly to recover and reuse expensive reagents and to control the discharge of chemicals into the wastewater. The solution obtained after precipitation of dissolved uranium as SDU contains significant amounts of sodium carbonate, sodium sulfate and residual sodium hydroxide.

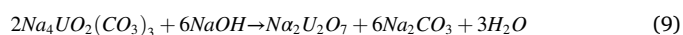
For the Gogi-type uranium ore several leaching options have been developed to maximize the extraction of uranium from the ore. The main process involves crushing and grinding to 90% by weight and grain size less than 74 μm , and alkaline leaching followed by solid-liquid separation and precipitation of a yellow precipitate as sodium diuranate (SDU). Under optimized precipitation conditions (temperature 50 $^{\circ}\text{C}$, reaction time 6 h) the purity of the precipitated sodium diuranate (SDU) was 82% U_3O_8 and the associated precipitation efficiency 97%, which corresponds to a total recovery of about 78%.

Kacham et al. (2014), performed the uranium leaching from carbonate minerals using sodium carbonate for leaching and oxygen as an oxidizing agent [55]. Alkaline leaching was performed because of the high carbonate content of the ore. Among the two commercial leaching solutions, Na_2CO_3 and $(\text{NH}_4)_2\text{CO}_3$, available for uranium mining, Na_2CO_3 was preferred for the low-silica Gogi uranium ore, while $(\text{NH}_4)_2\text{CO}_3$ was preferred for high-silica carbonate-type ores, as it is

highly selective for uranium and has a lower potential to dissolve silicate minerals. Furthermore, according to the authors, Na_2CO_3 is preferable as it is cheaper and more environmentally friendly than $(\text{NH}_4)_2\text{CO}_3$. Oxygen and air, although they react slower than other oxidants suitable for alkaline leaching, are preferred because of their cost and environmental friendliness. Following equation (Eq. 8) is a combination of the uranium oxidation present in the uranite/pitchblende and its subsequent carbonate-mediated dissolution.



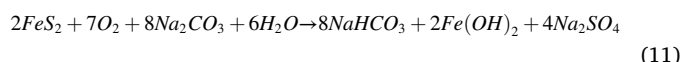
Increased hydroxide levels lead to the precipitation of uranium as $\text{Na}_2\text{U}_2\text{O}_7$ according to the following equation (Eq. 9):



In order to avoid precipitation $\text{Na}_2\text{U}_2\text{O}_7$, sodium bicarbonate is added, which neutralizes the hydroxides according to Eq. 10.

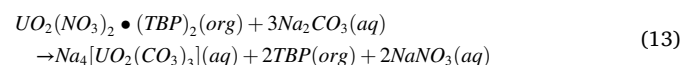
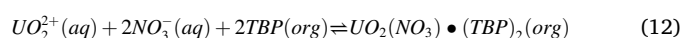


If the ore contains pyrite, addition of sodium bicarbonate may be not required, because sodium bicarbonate is produced in situ by the reaction of pyrite with sodium carbonate, as described by equation (Eq. 11).

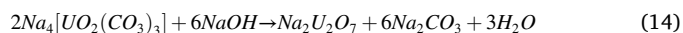


Generally, the uranium leaching rate increases when the agitation, sodium carbonate concentration and temperature increase. However, there is an optimum oxygen partial pressure, ranging between 0.5 atm and 1 atm at 90 $^{\circ}\text{C}$, where the maximum uranium dissolution (> 90%) and minimum pyrite dissolution (< 40%) occurs. Some older studies on carbonate leaching of uranium in autoclaves suggest that the rate of leaching is proportional to the square root of the oxygen partial pressure when everything else is kept constant. Moreover, according to Gilligan and Nikoloski (2021) pyrite is converted to iron hydroxides when ores containing pyrite are leached using alkaline carbonate solutions. Pyrite is destroyed after 24 h of leaching in 1 mol/L total carbonate at 90 $^{\circ}\text{C}$ [64].

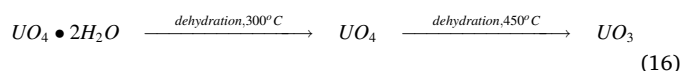
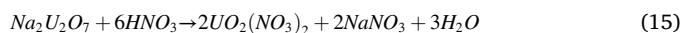
Uranium extraction using 25% tributyl phosphate, followed by the uranium recovery using 0.5 M sodium carbonate leads to a quantitative formation (> 98%) of the uranyl tricarbonate complex. The corresponding reactions are described by Eqs. 12 and 13.



Then uranium is precipitated as sodium diuranate precipitate ($\text{Na}_2\text{U}_2\text{O}_7$) by addition of 50% sodium hydroxide.



Further purification with nitric acid and calcination of the yellow cake leads to the formation of the orange uranium trioxide powder (UO_3) with an overall recovery rate of 93%. Eqs. 15 and 16 describe the associated reactions.



4.3. Ligand-mediated uranium recovery

Paschalidou and Pashalidis (2019), performed a relatively simple, efficient, selective, and low-cost method for the selective separation and determination of uranium in calcite and phosphogypsum samples

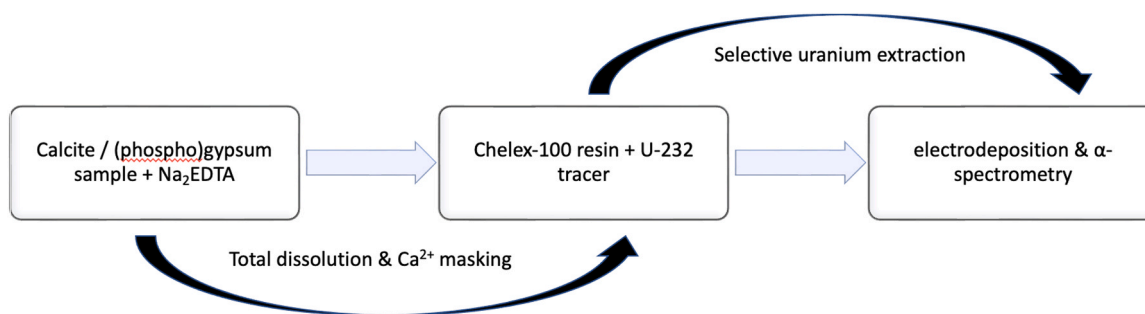
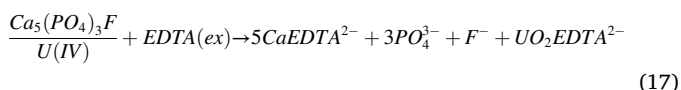


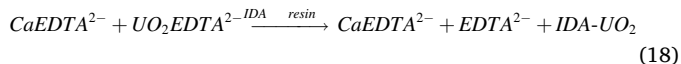
Fig. 7. : Schematic diagram of uranium recovery process from calcite and phosphogypsum.

(Fig. 7) [56]. The dissolution of the calcite and gypsum samples was performed by mixing 1 g of the powdered solids with 70 mL of 0.1 M Na_2EDTA . Then 1 g of resin was added and stirred for 2 h under ambient conditions and pH between 4.5 and 5. The resin was separated by filtration and then the uranium was eluted with 12 mL of 2 M HNO_3 solution. The separation efficiency of the method was $(75 \pm 10)\%$ and $(65 \pm 20)\%$ for gypsum and calcite samples, respectively.

Moreover, Paschalidou and Pashalidis (2019) in another publication, have applied a similar procedure to recover uranium from phosphorite with a yield rate of about 65% [27]. Phosphorite dissolution, which is described by Eq. 17, is favored due to the formation of the stable complexes CaEDTA^{2-} .



Following, a iminodiacetic resin (0.5 g Chelex@100) was added to the solution to selective binding uranium (U(VI)). Instead, calcium remains in solution as an EDTA complex (Eq. 18).



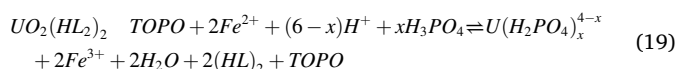
Following, uranium is leached from the resin with 2 M HNO_3 and can be recovered with the aid of a base as $\text{UO}_2(\text{OH})_2$, while the EDTA solution can be reused for the next dissolution procedure.

Bakry et al. (2021), studied the recovery of uranium from phosphates using also EDTA solutions [30]. The optimum conditions have been reached by using of 0.3 M EDTA combined with 0.05 M nitric acid, 40 g sample mass, mineral particle size 74 μm , solid liquid ratio $\frac{1}{4}$, 90 min contact time and continuous agitation at 25 $^\circ\text{C}$. An anion exchange resin was used to recover the uranium, which was then eluted from the resin by means of 1 M NaCl and acidification with 0.15 M H_2SO_4 . The eluate from the anion exchange resin (Duolite A 101D), was neutralized with sodium hydroxide (at pH 7) to precipitate sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$). The product was calcined at 750 $^\circ\text{C}$ for 1 h resulting in an uranium

recovery of 69.0% and a product purity of 91.9%.

Khaledi et al. (2019), selected a specific reagent that has a high efficiency regarding uranium elution from phosphate rocks (P_2O_5) [57]. The uranium is leached from the phosphate rocks and then separated from the slurry with an anion exchange resin. Prior elution all samples were crushed, washed with water and dried overnight at 105 $^\circ\text{C}$, in order to remove more than 80% of uranium and 5% of P_2O_5 from the phosphate rock. The first results were very encouraging, because by this elution process a large amount of REE and uranium is extracted without removing significant amounts of P_2O_5 from the ore. However, further experiments with different phosphate rocks as well as the application of the method in larger scale pilot plants are required.

Hurst et al. (1972) at Oak Ridge National Laboratory developed a two-cycle process with D_2EHPA –TOPO as solvents for the recovery of uranium from WPA (Wet Phosphoric Acid) [65]. This process uses a mixture of 0.5 mol L⁻¹ D_2EHPA and 0.125 mol L⁻¹ TOPO (Fig. 8) diluted in aliphatic kerosene. Uranium from WPA was first oxidized to U(VI) at 50 $^\circ\text{C}$ using NaClO_3 or air as oxidizing agents. The feed solution was then cooled to 40–45 $^\circ\text{C}$ before liquid–liquid extraction, because low temperature improves the extraction efficiency of U(VI) from D_2EHPA –TOPO. This four stage process recovers about 96% of the uranium from WPA. U(VI) is then reductively removed from the organic phase using 4–6 mol/L phosphoric acid in the presence of about 15 g/L Fe(II) at 50 $^\circ\text{C}$ according to Eq. 19.



The overbar indicates that the species are in the organic phase and the absence indicates species in aqueous phase. Generally, two or three steps are required to recover about 95% of the uranium from the extraction solution.

U(IV) is then oxidized to U(VI) by adding NaClO_3 or air to the aqueous solution at 70 $^\circ\text{C}$, followed by a second liquid-liquid extraction at 25–45 $^\circ\text{C}$ using 0.3 mol/L D_2EHPA and 0.075 mol/L TOPO. The extraction solvent is then cleaned with water at 25 $^\circ\text{C}$ and the uranium is

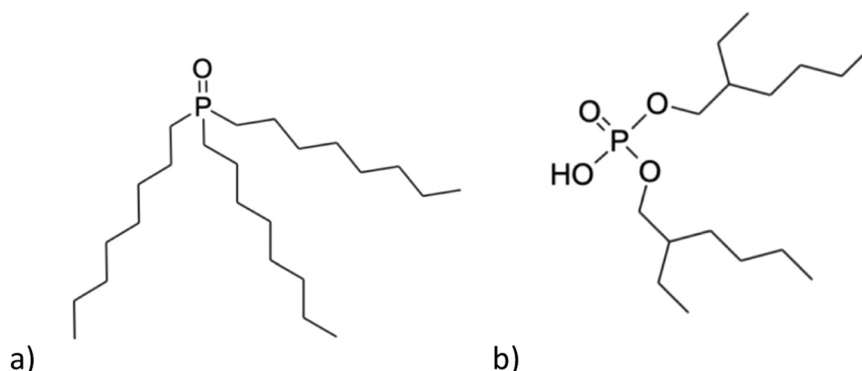
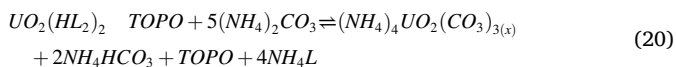


Fig. 8. Chemical structures of (a) TOPO and (b) D_2EHPA compounds.

removed using 2 mol/L ammonium carbonate, resulting in the direct precipitation of ammonium uranyl-tricarbonate with a about 99% yield, according to Eq. 20.



The precipitate is then filtered, washed with ammonia solution (NH_3), and then calcined to U_3O_8 .

Turgis et al. (2014) investigated the uranium recovery with an amino-phosphonate substituent from phosphoric acid, which is obtained using sulfuric acid from phosphate rocks [66]. This research was focused in the preparation and testing of compounds for the selective extraction of U(VI) from phosphoric acid solutions. After several studies it has been found that the HDEHP-TOPO synergistic mixture was the best combination of compounds because of their high stability and selectivity towards U(VI). However, synergistic mixtures are less reliable for industrial applications, while the use of a single molecule that combines the properties of the synergistic mixture is more promising. Thus, multifunctional molecules and specifically polyphosphate compounds (bisphosphonates or triphosphonates or triphosphonic acids) were designed and synthesized for the recovery of uranium from phosphoric acid (Fig. 9).

These systems showed significant extraction properties for U(IV) (0.07 M kerosene and 25–35% P_2O_5), but were not suitable for U(VI). In this case, reduction of U(VI) to U(IV) with Fe (0) is necessary. There is only one example of a suitable molecule using a bifunctional system to extract U(VI) from phosphoric acid. Warshawsky and Arad-Yelin synthesized a specific molecule combining a cation exchange moiety (phosphoric acid) and a neutral donor (phosphine oxide) separated by a polyether chain (Fig. 10).

Considering the above, bifunctional extractants bearing amide group and phosphoric acid group were synthesized (Fig. 11). These substituents possess and mimic the two properties of the synergistic HDEHP/TOPO mixture in one compound. The phosphonic acid group acts as a cation exchanger like HDEHP and the amino group can be considered as a donor group similar to TOPO in the synergistic system.

DEHCBPA (N,N-diethylhexylcarbamoybenzylphenylphosphonic acid), exhibits partition coefficient values twice those of the HDEHP/TOPO. The selectivity appears to be affected by the steric factor, and the modification of the electron density by introducing the phenyl group may also affect the interaction between the amide and phosphonate groups. The optimum amide group length appears to be a C8 chain, which is the optimum combination between a good separation and the solubility of organic molecules in the organic and aqueous phases.

Bakry (2021) in a recent study regarding the leaching of uranium from carbonate rocks, used a mixed reagent, citric acid and calcium citrate [29]. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) is a non-toxic tricarboxylic acid which forms complexes with various metal ions through carboxyl and hydroxyl groups. It is commonly used as a complexing agent to extract actinides, radionuclides and heavy metals from contaminated soils and minerals/rocks. Citric acid contains three carboxyl groups and one hydroxyl group that act as potential proton donors that can participate in the complexation/chelation of uranyl ions. The use of a citric acid/calcium citrate mixture in an appropriate solid/liquid ratio has been suggested for uranium leaching, because the presence of calcium citrate prevents

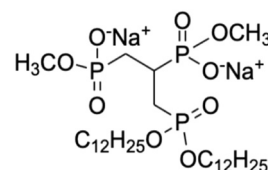
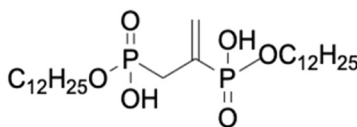
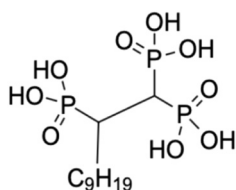


Fig. 9. Polyphosphate compounds for extraction of U(IV) from phosphoric acid [66].

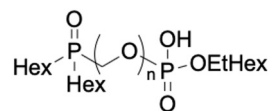


Fig. 10. Bifunctional molecule for the extraction of uranium(IV) from phosphoric acid.

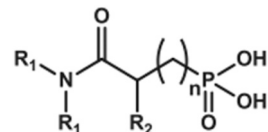
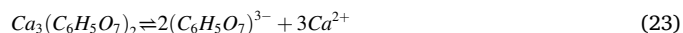
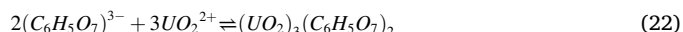


Fig. 11. Amido-phosphonate ligands.

the dissolution of calcium carbonate. The uranium is then recovered by addition of isopropyl alcohol. The individual equilibria in this system are described by the following reactions (Eqs. 21–23):



Various laboratory experiments were conducted to determine the performance of the citric acid/calcium citrate reagent mixture in the extraction of uranium from carbonate-rich black shale. The concentration of 0.06 M citric acid and calcium citrate in the mixed reagent was selected for selective leaching of uranium from black shale, and the relative results showed that citric acid effectively extracts uranium and the extraction efficiency increases with the concentration of citric acid, due to the complexation of U(VI) with citrates (UO_2HCit^-). The optimum particle size is 200 mesh ($\leq 74 \mu\text{m}$) and the highest leaching efficiency for uranium at observed at pH= 5.7.

A similar methodology was followed for the extraction of uranium from carbonate-rich black shale, in which the uranium exists in the form of uranyl dicarbonate metazellerite, $\text{Ca}(\text{UO}_2)(\text{CO}_3)2(\text{H}_2\text{O})_3$ and zellerite, $\text{Ca}(\text{UO}_2)(\text{CO}_3)2(\text{H}_2\text{O})_5$. The optimum conditions (uranium recovery ~95%) were found to be: citric acid/calcium citrate concentration 0.06 M, citric acid/Ca citrate molar ratio 1/1, grain size 200 mesh ($\leq 74 \mu\text{m}$), pH 5.7, S/L ratio 1/8, 75 min rinsing time and a temperature of 45 °C.

5. Conclusion and Perspectives

According to the existing literature, there are different methods for the extraction and recovery of uranium from carbonate and phosphate rocks and minerals. The extraction and recovery methods differ basically in the extraction of uranium from the solid matrix, which can be carried out by acidic, alkaline and ligand-mediated processes and the selective separation of uranium from the dissolution solution or leachate using uranium specific processes based on liquid-liquid extraction, ion-exchange or complexation. According to the studies the acid extraction of uranium is more efficient for most ores. On the other hand,

alkaline and ligand-mediated dissolution of uranium is slower compared the dissolution rates associated with acidic dissolution. Nevertheless, former extraction methods lead to a better quality and purity precipitate in the product recovery stage.

Considering the aforementioned studies, it becomes clear that there is a need for further investigations to apply environmentally friendly ligands for the successful recovery of uranium from ores. These investigations could include the use ligands such as sodium citrate or sodium nitrilotriacetate (NTA), under slightly acidic conditions for the recovery of uranium from carbonate and phosphate rocks and minerals. Moreover, in addition to the recovery of uranium and phosphates from rocks/minerals, the recovery and recycling complexing agents from the process solutions is also of particular interest.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

References

- [1] I. Ioannidis, V. Kinigopoulou, D. A. Giannakoudakis, M. Arkas, I. Anastopoulos, K. S. Triantafyllidis, I. Pashalidis, Microplastics and disposable face masks as "Trojan Horse" for radionuclides pollution in water bodies—a review with emphasis on the involved interactions, *Sustain. Chem. Environ.* (2023), 100005.
- [2] R. Nieder, D.K. Benbi, F.X. Reichl, Health risks associated with radionuclides in soil materials, *Soil Compon. Hum. Health* (2018) 451–501.
- [3] Z. Altschuler, R.S. Clarke Jr, E. Young, Shorter contributions to general geology, *Geol. Surv. Prof. Paper*, 45 (1959) 314.
- [4] H. Khoury, Uranium minerals of central Jordan, *Appl. Earth Sci.* 124 (2) (2015) 104–128.
- [5] D.M. Singer, F. Farges, G.E. Brown Jr, Biogenic nanoparticulate UO₂: synthesis, characterization, and factors affecting surface reactivity, *Geochim. Et. Cosmochim. Acta* 73 (12) (2009) 3593–3611.
- [6] G. Meinrath, Coordination of uranyl (VI) carbonate species in aqueous solutions, *J. Radioanal. Nucl. Chem.* 211 (2) (1996) 349–362.
- [7] S.A. Kobets, G.N. Pshinko, L.N. Puzyrnaya, Uranium (VI) in natural waters: study of occurrence forms, *J. Water Chem. Technol.* 34 (2012) 277–283.
- [8] M. Lysandrou, I. Pashalidis, Uranium chemistry in stack solutions and leachates of phosphogypsum disposed at a coastal area in Cyprus, *J. Environ. Radioact.* 99 (2) (2008) 359–366.
- [9] K. Cantrell, J.M. Zachara, P.E. Dresel, K. Krupka, R. Serne, Geochemical Processes Data Package for the Vadose Zone in the Single-Shell Tank Waste Management Areas at the Hanford Site (2023).
- [10] W. Tan, F. Guo, Q. Deng, J. Li, L. Wang, The effects of *Leifsonia* sp. on bioavailability and immobilization mechanism of uranium in soil, *J. Soils Sediment.* 20 (2020).
- [11] F. Papanicolaou, S. Antoniou, I. Pashalidis, Experimental and theoretical studies on physico-chemical parameters affecting the solubility of phosphogypsum, *J. Environ. Radioact.* 100 (10) (2009) 854–857.
- [12] D. Tendall, C. Binder, Nuclear energy in Europe: uranium flow modeling and fuel cycle scenario trade-offs from a sustainability perspective, *Environ. Sci. Technol.* 45 (6) (2011) 2442–2449.
- [13] F. Gao, M. Li, X. Zhang, C. Huang, X. Wu, Y. Zhou, Q. Fang, Liberation mechanism of uranium from radioactive metallurgical waste containing uranium by a clean leaching method, *JOM* 72 (10) (2020) 3491–3501.
- [14] E. Marsili, H. Beyenal, L. Palma, C. Merli, A. Dohnalkova, J. Amonette, Z. Lewandowski, Uranium immobilization by sulfate-reducing biofilms grown on hematite, dolomite, and calcite, *Environ. Sci. Technol.* 41 (24) (2007) 8349–8354.
- [15] C. Karakosta, C. Pappas, V. Marinakis, J. Psarras, Renewable energy and nuclear power towards sustainable development: characteristics and prospects, *Renew. Sustain. Energy Rev.* 22 (2013) 187–197.
- [16] J. Morales Pedraza, J. Morales Pedraza, The Current Situation and Perspectives on the Use of Nuclear Energy for Electricity Generation, in *Electrical Energy Generation in Europe: The Current Situation and Perspectives in the Use of Renewable Energy Sources and Nuclear Power for Regional Electricity Generation*, (2015) 421–629.
- [17] M. Ho, E. Obbard, P.A. Burr, G. Yeoh, A review on the development of nuclear power reactors, *Energy Procedia* 160 (2019) 459–466.
- [18] A.N. Creager, Nuclear energy in the service of biomedicine: the US atomic energy commission's radioisotope program, 1946–1950, *J. Hist. Biol.* 39 (2006) 649–684.
- [19] R.U. Ayres, Nuclear Power, in *The History and Future of Technology: Can Technology Save Humanity from Extinction?*, (2021) 589–621.
- [20] J.W. Eerkens, Electric Power Generation Technology, in *The Nuclear Imperative: A Critical Look at the Approaching Energy Crisis*, (2006) 69–95.
- [21] B. Van der Zwaan, Prospects for nuclear energy in Europe (Issues), *Int. J. Glob. Energy* 30 (1–4) (2008) 102–121.
- [22] M. Nezhad, A. Semnani, N. Tavakkoli, M. Shirani, Efficient removal and recovery of uranium from industrial radioactive wastewaters using functionalized activated carbon powder derived from zirconium carbide process waste, *Environ. Sci. Pollut. Res.* 28 (40) (2021) 57073–57089.
- [23] S. Song, K. Wang, Y. Zhang, Y. Wang, C. Zhang, X. Wang, R. Zhang, J. Chen, T. Wen, X. Wang, Self-assembly of graphene oxide/PEDOT:PSS nanocomposite as a novel adsorbent for uranium immobilization from wastewater, *Environ. Pollut.* 250 (2019) 196–205.
- [24] C.K. Gupta, H. Singh, Uranium resource processing, Springer, Berlin, 2001.
- [25] E. AbowSlama, E. Ebraheem, A. Sam, Precipitation and purification of uranium from rock phosphate, *J. Radioanal. Nucl. Chem.* 299 (1) (2013) 815–818.
- [26] G.T. Nwaila, H.E. Frimmel, S.E. Zhang, J.E. Bourdeau, L.C. Tolmay, R.J. Durrheim, Y. Ghorbani, The minerals industry in the era of digital transition: an energy-efficient and environmentally conscious approach, *Resour. Policy* 78 (2022), 102851.
- [27] P. Paschalidou, I. Pashalidis, Recovery of uranium from phosphate rock with EDTA-mediated dissolution and cation exchange, *Hydrometallurgy* 189 (2019), 105118.
- [28] T. Bakalár, H. Pavolová, Z. Šimková, L. Bednářová, Phosphorus management in Slovakia—a case study, *Sustainability* 14 (16) (2022) 103.
- [29] A. Bakry, M. Demerdash, E. Manaa, A. Fatah, Recovery of uranium and rare earth elements from western desert phosphate rocks with EDTA and nitric acid solutions, *Radiochemistry* 63 (3) (2021) 297–306.
- [30] P.J. Withers, J.J. Elser, J. Hilton, H. Ohtake, W.J. Schipper, K.C. Van Dijk, Greening the global phosphorus cycle: how green chemistry can help achieve planetary P sustainability, *Green. Chem.* 17 (4) (2015) 2087–2099.
- [31] H. Tulsidas, S. Gabriel, K. Kiegiel, N. Haneklaus, Uranium resources in EU phosphate rock imports, *Resour. Policy* 61 (2019) 151–156.
- [32] J. Lin, W. Sun, J. Desmarais, N. Chen, R. Feng, P. Zhang, D. Li, A. Lieu, J. Tse, Y. Pan, Uptake and speciation of uranium in synthetic gypsum (CaSO₄·2H₂O): applications to radioactive mine tailings, *J. Environ. Radioact.* 181 (2018) 8–17.
- [33] H. Tayibi, M. Choura, F. López, F. Alguacil, A. López-Delgado, A., Environmental impact and management of phosphogypsum, *J. Environ. Manag.* 90 (8) (2009) 2377–2386.
- [34] G. Andreou, M. Efstathiou, I. Pashalidis, A simplified determination of uranium in phosphate rock and phosphogypsum by alpha-spectroscopy after its separation by liquid-extraction, *J. Radioanal. Nucl. Chem.* 291 (3) (2011) 865–867.
- [35] H. Tayibi, M. Choura, F.A. López, F.J. Alguacil, A. López-Delgado, Environmental impact and management of phosphogypsum, *J. Environ. Manag.* 90 (8) (2009) 2377–2386.
- [36] S. Iliadou, A. Tsirambidis, A. Kasoli-Fournarakis, K. Michailidis, Petrographic and geochemical research of the carbonate rocks of the area of Vafiochori Kiliks, *Bull. Geol. Soc. Greece* 36 (1) (2004) 10.
- [37] K. Bell, Uranium in carbonate rocks, U.S. Gov. Print. Off. (1963).
- [38] T. Sreenivas, J. Chakravarty, Alkaline processing of uranium ores of Indian origin, *Trans. Indian Inst. Met.* 69 (1) (2015) 3–14.
- [39] A.Z.M. Abouzeid, Physical and thermal treatment of phosphate ores—an overview, *Int. J. Miner. Process.* 85 (4) (2008) 59–84.
- [40] P. Nolan, S. Bone, K. Campbell, D. Pan, O. Healy, M. Stange, J. Bargar, K. Weber, Uranium(VI) attenuation in a carbonate-bearing oxic alluvial aquifer, *J. Hazard. Mater.* 412 (2021), 125089.
- [41] L.F. Silva, M.L. Oliveira, T.J. Crissien, M. Santosh, J. Bolivar, L. Shao, Guilherme L. G. Dotto, J. Dotto, M. Schindler, A review on the environmental impact of phosphogypsum and potential health impacts through the release of nanoparticles, *Chemosphere* 286 (2022), 131513.
- [42] Y. Chernysh, O. Yakhnenko, V. Chubur, H. Roubík, Phosphogypsum recycling: a review of environmental issues, current trends, and prospects, *Appl. Sci.* 11 (4) (2021) 1575.
- [43] E. Saadaoui, N. Ghazel, C. Ben Romdhane, N. Massoudi, Phosphogypsum: potential uses and problems—a review, *Int. J. Environ. Stud.* 74 (4) (2017) 558–567.
- [44] S.V. Krivovichev, J. Plášil, P.C. Burns, G.E. Sigmon, Mineralogy and crystallography of uranium, in *Uranium: From Cradle to Grave*, Mineral. Assoc. Can. Short. Courses 43 (2013) 15–119.
- [45] B. Mishra, N.R. Gubel, R. Bhola, Uranium processing, *Uranium Process. Prop.* (2013) 123–172.
- [46] F. Santos-Francés, E.G. Pacheco, A. Martínez-Grana, P.A. Rojo, C.Á. Zarza, A. G. Sánchez, Concentration of uranium in the soils of the west of Spain, *Environ. Pollut.* 236 (2018) 1–11.
- [47] P.L. Smedley, D.G. Kinniburgh, Uranium in natural waters and the environment: distribution, speciation and impact, *Appl. Geochem.* 105534 (2022).
- [48] T. Sreenivas, J.K. Chakravarty, Alkaline processing of uranium ores of Indian origin, *Trans. Indian Inst. Met.* 69 (2016) 3–14.
- [49] K. Kiegiel, A. Miskiewicz, D. Gajda, S. Sommer, S. Wolkowicz, G. Zakrzewska-Koltuniewicz, Uranium in Poland: resources and recovery from low-grade ore, *Uranium* (2018) 65–88.
- [50] K. Kiegiel, A. Miskiewicz, D. Gajda, S. Sommer, S. Wolkowicz, G. Zakrzewska-Koltuniewicz, Uranium in Poland: resources and recovery from low-grade ores, *Sep. Sci. Technol.* 55 (12) (2021) 1–9.
- [51] A. Bakry, An alternative procedure for selective leaching of uranium from carbonate-rich black shale, um-bogma formation, El-Allouga, Southwestern Sinai, 2021, *Radiochemistry* 63 (1) (2021) 87–95.

- [52] A. Adam, M. Eltayeb, O. Ibrahim, Uranium recovery from Uro area phosphate ore, Nuba Mountains, Sudan, Arab. J. Chem. 7 (5) (2014) 758–769.
- [53] E. Guzmán, E. Regil, G. Pacheco-Malagon, G. Uranium, leaching from phosphate rock, J. Radioanal. Nucl. Chem. Lett. 201 (4) (1995) 313–320.
- [54] H. Shlewit, M. Alibrahim, Recovery of uranium from phosphate by carbonate solutions, J. Radioanal. Nucl. Chem. 275 (1) (2007) 97–100.
- [55] A. Kacham, A. Suri, A. Application of a topochemical reaction model to predict leaching behavior of high carbonate uranium ores in alkaline solutions: an experimental case study, Hydrometallurgy 141 (2014) 67–75.
- [56] P. Paschalidou, I. Pashalidis, Selective separation and determination of uranium in calcite and gypsum after EDTA-mediated sample dissolution and cation-exchange, J. Radioanal. Nucl. Chem. 320 (3) (2019) 807–812.
- [57] N. Al Khaledi, M. Taha, A. Hussein, E. Hussein, A. El Yahyaoui, N. Haneklaus, Direct leaching of rare earth elements and uranium from phosphate rocks, IOP Conference Series: Materials Science and Engineering, 479 (2019) 012065.
- [58] B.I. Whittington, D. Muir, Pressure acid leaching of nickel laterites: a review, Miner. Process. Extr. Metallurgy Rev. 21 (6) (2000) 527–599.
- [59] W. Zhang, R. Honaker, Calcination pretreatment effects on acid leaching characteristics of rare earth elements from middlings and coarse refuse material associated with a bituminous coal source, Fuel 249 (2019) 130–145.
- [60] C. Castillo, P. Fawell, A. Costine, Optimising the activity of acrylamide-based polymer solutions used to flocculate mineral processing tailings suspensions—a review, Chem. Eng. Res. Des. 199 (2023) 214–237.
- [61] D. Beltrami, G. Cote, H. Mokhtari, B. Courtaud, B.A. Moyer, A. Chagnes, A. Recovery of uranium from wet phosphoric acid by solvent extraction processes, Chem. Rev. 114 (24) (2014) 12002–12023.
- [62] K. Weterings, J. Janssen, Recovery of uranium, vanadium, yttrium and rare earths from phosphoric acid by a precipitation method, Hydrometallurgy 15 (2) (1985) 173–190.
- [63] B.J. Youlton, J.A. Kinnaird, Gangue–reagent interactions during acid leaching of uranium, Miner. Eng. 52 (2013) 62–73.
- [64] R. Gilligan, A.N. Nikoloski, The effects of phosphate gangue on the leaching of uranium from brannerite, Mining Metall. Explor. 38 (2021) 763–773.
- [65] F. Hurst, D. Crouse, K. Brown, Recovery of uranium from wet-process phosphoric acid, Ind. Eng. Chem. Process Des. Dev. 11 (1) (1972) 122–128.
- [66] R. Turgis, A. Leydier, G. Arrachart, F. Burdet, S. Dourdain, G. Bernier, M. Miguiditchian, S. Pellet-Rostaing, Uranium extraction from phosphoric acid using bifunctional amido-phosphonic acid ligands, Solvent Extr. Ion.-. Exch. 32 (5) (2014) 478–491.