

Uranium as a renewable for nuclear energy



Claude Degueudre ^{a, b, *}

^a NES, Paul Scherrer Institute, 5232 Villigen, Switzerland

^b ChiAM, Université de Genève, q. E. Ansermet 30, 1211 Genève, Switzerland

ARTICLE INFO

Article history:

Received 24 September 2015

Received in revised form

19 February 2016

Accepted 31 March 2016

Available online 25 May 2016

Keywords:

Uranium

Resources

Nuclear energy

Sea water

Renewable

ABSTRACT

Uranium extraction is the first step of the nuclear fuel cycle. Currently, uranium is only extracted from solid ores such as uranium rich minerals (% level) or minerals such as phosphates (ppm level). For some years extraction of uranium from sea water (ppb level) has been the topic of investigations particularly in Japan due to its national interest. In the huge oceanic volume the amount of uranium is constant, regulated by its river input (soluble) and balanced by its scavenging (particulate) on the sea floor. This work shows that the uranium extraction with parsimony from sea water could be carried in a renewable way if its concentration remains quasi constant. Recommendations for the extraction with use of gel panels or with braid of fabric grafted by sorbing groups in high tide or oceanic pelagic current environments are suggested along with a reduction of the uranium consumption.

© 2016 Published by Elsevier Ltd.

1. Introduction

Presently, the uranium needs are evaluated for today's reactor fleet totaling 430 units to be 65,000 t of originally natural uranium a year (Emsley, 2014). This current demand is mostly filled by uranium production which is mostly issued from the mining exploitation of ores whose contents range from say about 50 (or more) to 0.05 wt% e.g. Frondel and Fleisher, 1950; Nininger, 1954.

The International Atomic Energy Agency (IAEA) assigns uranium deposits as types, based on their geological setting and genesis of mineralization. These deposits are arranged according to their approximate economic significance from high to relatively lower uranium fraction.

Primary uranium minerals are uraninite or pitchblende UO_2 , coffinite $\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$ and brannerite (UTi_2O_6) with uranium fractions of 88.1, 70.4 and 59.8 wt% respectively. The secondary uranium minerals are autunite $(\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \times 8-12 \text{H}_2\text{O})$, carnotite $(\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \times 1-3 \text{H}_2\text{O})$, torbernite $(\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \times 12 \text{H}_2\text{O})$ and uranophane $(\text{Ca}(\text{UO}_2)_2(\text{HSiO}_4)_2 \times 5 \text{H}_2\text{O})$ and with respective uranium fraction below 50 wt%.

Deposits also include uranium containing formations of sandstone, quartz, phosphorite, lignite and black shale deposits, locally in form of breccia, veins metamorphic, intrusive or volcanic. Here

the uranium fraction decreases below 1 wt% and exploitation can be extended to fractions dropping to the 0.01 wt% level.

The extraction practice is widely established with various strategies ranging from the excavation in open pit (OP) e.g. in Namibia, Niger and Australia to deep tunneling (underground, UG) such as in Canada or Russia, through ore rich formations. In addition to physical exploitation, chemical treatments such as in situ leaching (ISL) may be used as in Kazakhstan. The largest-producing uranium mines in 2013 were: McArthur River, Canada (13%, UG), Olympic Dam, Australia (6%, UG), Somair, Niger (5% OP), Tortukuduk, Kazakhstan (4%, ISL), Priargunsky, Russia (4%, UG) Langer Heinrich, Namibia (4%, OP) and Ranger, Australia (4%, OP), producing a total of 59 kt (100%). The global nuclear fuel market reached a total world production of 59,370 t of U (or 70,015 t of U_3O_8) that is 92% of the worlds demand (WNA, 2013).

The uranium in term of U_3O_8 production has in the meantime increased steadily from 47 kt in 2006 to 70 kt in 2013 (See Fig. 1). The demand could, however, reach 100 kt with today's nuclear fuel cycle practice i.e. open cycle (mostly) with light water reactors (LWR).

Uranium exploitation may be performed as long as the extraction is economically viable whilst also considering ecological issues. The known recoverable uranium resources were evaluated reaching a total of 5.5 Mt (OECD, 2011, 2014). Basically countries such as Australia, Kazakhstan, Russia, Canada and Niger are key players while 9 other countries well spread in the world have significant potential (above 1%).

* Engineering Department, Lancaster University, Lancaster, LA1 4YW, UK.
E-mail address: claudedegueudre@unige.ch.

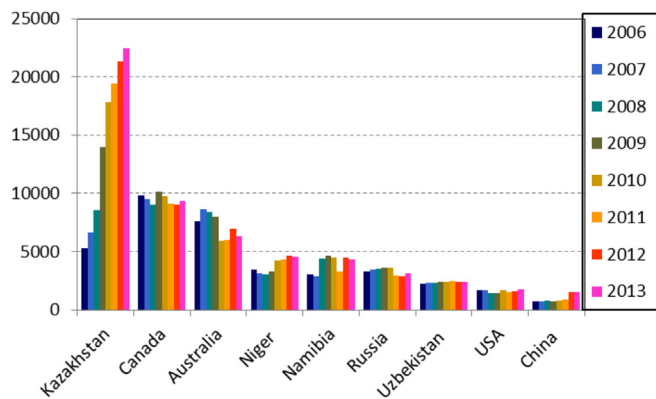


Fig. 1. Comparison of uranium annual productions from various countries over the last 8 years. Note the rather constant production of UG and OP countries while ISL has increased Kazakhstan production by a factor 4 during the 8 years.

The reasonably assured resources, at US\$ 130 per kg of U, (Australia 31%, Kazakhstan 12%, Russia 9%, Canada 9%, Niger 8%, South Africa 5%, Brazil 5%, Namibia 5%, USA 4% and China 3%), would be 5,327,200 tons of U (OECD, 2011). The total at US\$ 260 per kg of U is 7,096,600 tons U, and Namibia moves up ahead of Niger. The total resources were reevaluated recently (OECD, 2014) suggesting a 10% increase compared to 2011.

In addition to the 5.4 million tons of uranium in known recoverable resources, there are substantial amounts comprising what are known as “unconventional resources”.

For about 50 years the extraction of uranium from large **phosphate** deposits has been proposed as an alternative production. The U content in the phosphate ores currently ranges from 10 to 100 ppm and the U extraction has been applied as a purification step (decontamination) e.g. Hurst 1989. Prayon, Belgium (Davister and Martin, 1989) has applied this extraction over about 20 years (1978–1998). In 1998 the extraction was discontinued because the uranium price was too low. Consequently, Prayon changed the import source of phosphate towards less U rich ores. The world phosphate annual production includes China (65 Mt), Morocco & W Sahara (26 Mt), USA (26 Mt), Tunisia (7.6 Mt), Jordan (6 Mt), Brazil (5.5 Mt) and Egypt (5 Mt) as top producers. The world production reached 176×10^6 t per year in 2010. With an extraction of the 30 ppm level of uranium the production could reach potentially 5×10^3 t a⁻¹. Estimates of the available total uranium amounts range from 9 to 22 (average 15) Mt.

Also among the “unconventional resources” are **coal** derived products such as fly ash. The best estimates of the total amount of coal (including undiscovered coal) in the world are about 12 trillion tons (Devereux Carter, 1976) i.e. 12×10^{12} t. The total of U resource includes several categories of coal with various degrees of geologic assurance and data reliability. If one estimates the average uranium concentration to be 5 ppm then a total amount of 6×10^7 t of U may be derived from these values. Uranium from coal residues is a topic of R&D in various countries. As an example Mongolia uranium recovery from coal ash dumps has been recently investigated (Maslov et al., 2010). Decontamination (U, Th and decay products) of the

ashes for other uses (building material) is an important point and the recovery of uranium is also possible. With the coal mining rate of 10^9 t a⁻¹ and an extraction of the 5 ppm level of uranium the production could also reach potentially 5×10^3 t a⁻¹.

These extractions from solid ores and as by-products cannot be labeled as renewable. In addition since the ore treatment induces potential releases of natural radioelements and of chemical reagents they generate tailings that must be managed carefully.

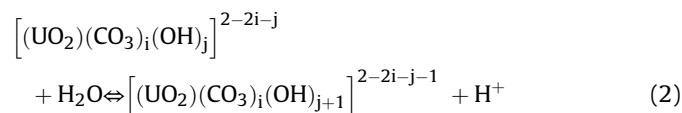
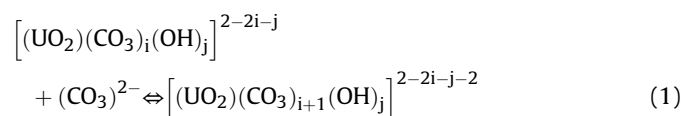
Renewable energy is derived from natural processes that are replenished constantly. Included in the definition is heat generated, electricity and derived hydrogen from sunlight, wind, oceans, hydropower, biomass, geothermal resources and biofuels. From today's nuclear fuel cycle options it may be shown that with the practice of reprocessing and recycling as well as with the use of actinide as burnable poison, nuclear energy could be qualified sustainable. However, from sustainable to renewable the need of a refurbishable source of fuel is required such as for biomass. In this work uranium in sea water is revisited focusing on the very large source properties with assured replenishment. This concept was already suggested and approached in a semi-quantitative way for example by Cohen, 1983. The purpose of this review and contribution study is to investigate and assess the limitations on the extraction of uranium from the sea and on its use to gain the label renewable.

2. Phenomenological approach

To understand the behaviour of uranium in the sea water it is important to depict its speciation including its sorption on particles prior to evaluating the input and output fluxes from the dissolved state that yield a quasi-equilibrium state in the sea.

2.1. Uranium speciation in aquatic systems

Starting with U(VI) as uranium redox state and UO_2^{2+} as basic species, the complex species that form in aqueous solution are hydroxide and carbonate complexes Ref. Saito and Miyauchi (1982) and Djogic et al. (1986). Uranyl complexes with fluoride – sulphate – phosphate and organics, e.g. oxalate, are ignored because of the low ligand concentration or their low complexation constant. The discrete formation reactions of the hydroxide – carbonate mixed complexes are:



The carbonate-, hydroxide- and mixed complex concentration can be quantified using the stability constants (partial: K or cumulative: β) according to the following equations:

$$K_{(i+1,j)} = \left[[(\text{UO}_2)(\text{CO}_3)_{i+1}(\text{OH})_j]^{2-2i-j-2} \right] \left[[(\text{UO}_2)(\text{CO}_3)_i(\text{OH})_j]^{2-2i-j} \right]^{-1} \left[(\text{CO}_3)^{2-} \right]^{-1} \quad (3)$$

$$K_{(ij+1)} = \left[\left[(\text{UO}_2)(\text{CO}_3)_i(\text{OH})_{j+1} \right]^{2-2i-j-2} \right] [\text{H}^+] \left[\left[(\text{UO}_2)(\text{CO}_3)_i(\text{OH})_j \right]^{2-2i-j-1} \right] [(\text{OH})^-]^{-1} \quad (4)$$

and

$$\beta(i, j) = \Pi K_{(ij)} \quad (5)$$

Calculations of the species concentrations in aquatic systems can be carried out using thermodynamic codes. In this work the data are selected from [Ball and Nordstrom \(1992\)](#) compilations and completed with recent specific data for ternary complexes e.g. [Maloubier et al., 2015](#).

The average uranium concentration in sea water is reported to be around 3.3 ppb. It is compared to other elements in sea water in [Fig. 2](#). For the total volume of sea water (1.37 billion km³), see [Whitfield \(1979\)](#), the uranium amount would be about 4.5 billion tons e.g. [Bardi \(2010\)](#). This is about 1000 times greater than the amount of U contained in the surface of sea floor.

2.1.1. Uranium in sea water

The uranium concentration in sea water may be compared with that of the other elements. A comparison is given in [Fig. 2](#). The elements and species needed for speciation calculation are given in [Table 1a](#).

Speciation modeling of the U soluble part shows that the major fraction is the tri-carbonate uranyl oxoanion: $((\text{UO}_2)(\text{CO}_3)_3)^{4-}$. Thermodynamic calculations for uranium in sea water were performed for $p_e = 8.45$, ionic strength 6.748×10^{-1} , a total carbon = 2.18×10^{-3} M, total $\text{CO}_2 = 2.18 \times 10^{-3}$ M, temperature = 25.0 °C. The temperature is fixed at 25 °C for standardization in the comparison such as tested earlier e.g. [Whitfield \(1975\)](#). Even if this temperature is larger than the average surface water, this is the temperature of the water where U extraction is recommended. However for information the first U(VI) sorbing species $((\text{UO}_2)(\text{CO}_3)_2)^{2-}$ increases in concentration from 4.5×10^{-12} to 18.4×10^{-12} M when the temperature increases from 0 to 30 °C.

In these conditions the uranium species concentrations are given in [Table 1b](#). It must be noted that the soluble tricarbonatate species would include $[\text{Ca}_2\text{UO}_2(\text{CO}_3)_3]$ (1%, $\log \beta = 29.22$), $[\text{CaUO}_2(\text{CO}_3)_3]^{-2}$ (41%, $\log \beta = 27.18$), $\text{Mg}[\text{UO}_2(\text{CO}_3)_3]^{-2}$ (18%, $\log \beta = 26.11$) and $[\text{UO}_2(\text{CO}_3)_3]^{-4}$ itself (40%, $\log \beta = 21.84$) such as reported by [Maloubier et al., 2015](#).

The saturation index for uraninite (UO_2) is -12.67 and no precipitation of the uranium dioxide is expected for the redox potential of the sea water (oxidising).

2.1.2. Uranium speciation in river water

The speciation is performed as an example in the case of Amazon water: the largest river in the world. Its water chemical composition varies seasonally, although an average around Manaus may be estimated, see [Table 2a](#).

The speciation results are given in [Table 2b](#). The speciation of the soluble part shows that the major fraction is the tri-carbonate uranyl oxoanion: $((\text{UO}_2)(\text{CO}_3)_3)^{4-}$. However, significant fractions

Table 1

Water chemistry data from seawater (concentrations in M). **a-** Input data. **b-** Calculation output data as calculated using thermodynamic data base ([Ball and Nordstrom \(1992\)](#)).

| a Input [] | (M) |
|--|-------------------------|
| pH | 8.2 |
| Na | 4.7×10^{-1} |
| K | 1.0×10^{-2} |
| Mg | 5.3×10^{-2} |
| Ca | 1.0×10^{-2} |
| HCO ₃ | 2.0×10^{-3} |
| Cl | 5.5×10^{-1} |
| SO ₄ | 2.8×10^{-2} |
| U | 1.5×10^{-8} |
| b Output [] | (M) |
| U(IV) | $<1.00 \times 10^{-20}$ |
| U(V) UO ₂ ⁺ | 1.62×10^{-18} |
| U(VI) | 1.43×10^{-8} |
| ^a UO ₂ (CO ₃) ₃ ⁴⁻ | 1.25×10^{-8} |
| UO ₂ (CO ₃) ₂ ²⁻ | 1.81×10^{-9} |
| UO ₂ CO ₃ | 7.42×10^{-12} |
| UO ₂ OH ⁺ | 3.38×10^{-14} |
| UO ₂ ²⁺ | 3.01×10^{-16} |

^a All tricarbonatate complexes (binary and ternary) see text.

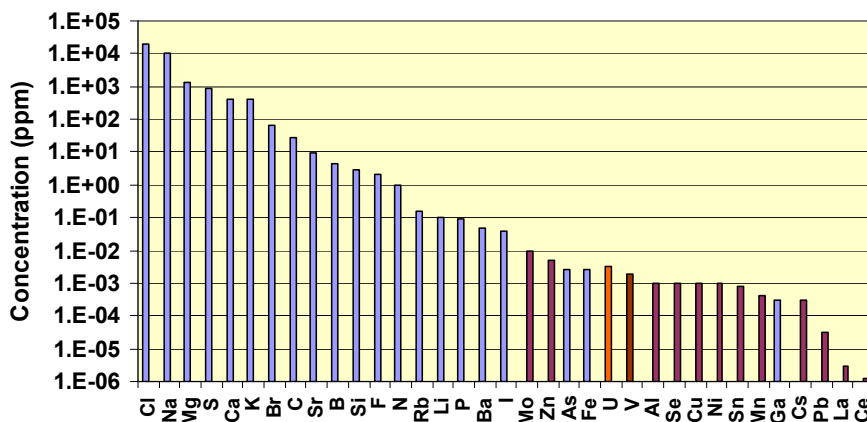


Fig. 2. Elements in seawater ([Millero, 2013](#)) in red extractable metal of direct interest, in orange U. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

Table 2

Water chemistry data from Amazon River (concentrations in M). Note the Amazon water is sampled in Manaus Ref. Gaillardet et al., 1997. **a**- Input data. **b**- Calculation output data (Data base Ball and Nordstrom (1992))

| a input [] | (M) |
|--|------------------------|
| pH | 7.1 |
| Na | 1×10^{-4} |
| K | 2×10^{-5} |
| Mg | 5×10^{-5} |
| Ca | 2×10^{-4} |
| HCO ₃ | 5×10^{-4} |
| Cl | 7×10^{-4} |
| SO ₄ | 2×10^{-7} |
| U | 1.6×10^{-10a} |
| b Output [] | (M) |
| U(IV) | $<1.0 \times 10^{-20}$ |
| U(V) UO ₂ ⁺ | 2.50×10^{-18} |
| U(VI) | 1.58×10^{-10} |
| *UO ₂ (CO ₃) ₃ ⁴⁻ | 7.30×10^{-11} |
| UO ₂ (CO ₃) ₂ ²⁻ | 4.60×10^{-11} |
| UO ₂ CO ₃ | 3.75×10^{-11} |
| UO ₂ OH ⁺ | 1.28×10^{-12} |
| UO ₂ ²⁺ | 4.50×10^{-16} |

Note *Uranium concentration in Amazon River water filtrate <0.45 μm (it includes the colloidal part).

^a All tricarbonat complexes (binary and ternary) see text.

of both UO₂(CO₃)₂²⁻ and UO₂CO₃ are now present mostly due to the lower pH which may modify their behaviour in the river water. It

must also be noted that the soluble tri-carbonate species would include Ca₂[UO₂(CO₃)₃] (1.6%), Ca[UO₂(CO₃)₃]²⁻ (92.8%) and Mg [UO₂(CO₃)₃]²⁻ (2.0%) together with [UO₂(CO₃)₃]⁴⁻ (3.7%), e.g. Prat et al., 2009.

2.1.3. Comparing uranium speciation in sea and river water

A comparison of the uranium species in sea and river waters may explain the behaviour difference of U in both aquatic systems (see Fig. 3a for sea and Amazon River waters and Fig. 3b for various pH waters). Clearly, in sea water the tri-carbonate complexes are dominant, at over 85%, while in river water even if the tri-carbonate is still dominant, both bi- and mono-carbonate complexes reach 30% and 22% respectively in Amazon River water. This should be expected in neutral to weakly basic river water e.g. pH 6.8–7.8 (as reported by Nikanorov and Brazhnikova, 2002) suggesting stronger potential for sorption in non basic river water with consequent U elimination by particle scavenging mechanism for example. This has to be investigated in more details.

2.2. Sorption of uranium on particulate in aquatic systems

Sorption on so called “dirty” particles is driven by feranol groups (>FeOH sites) from iron oxy-hydroxide coatings, masking original aluminol groups (>AlOH sites, strongly sorbing) and silanol groups (≥SiOH sites, weakly sorbing) on clay for example for inorganic colloids or original carboxyl groups (–COOH sites, mildly sorbing) on organics or bioorganic features.

The reaction that describes the sorption by surface complexation of a hydroxide carbonate mixed complex on feranol model site is:

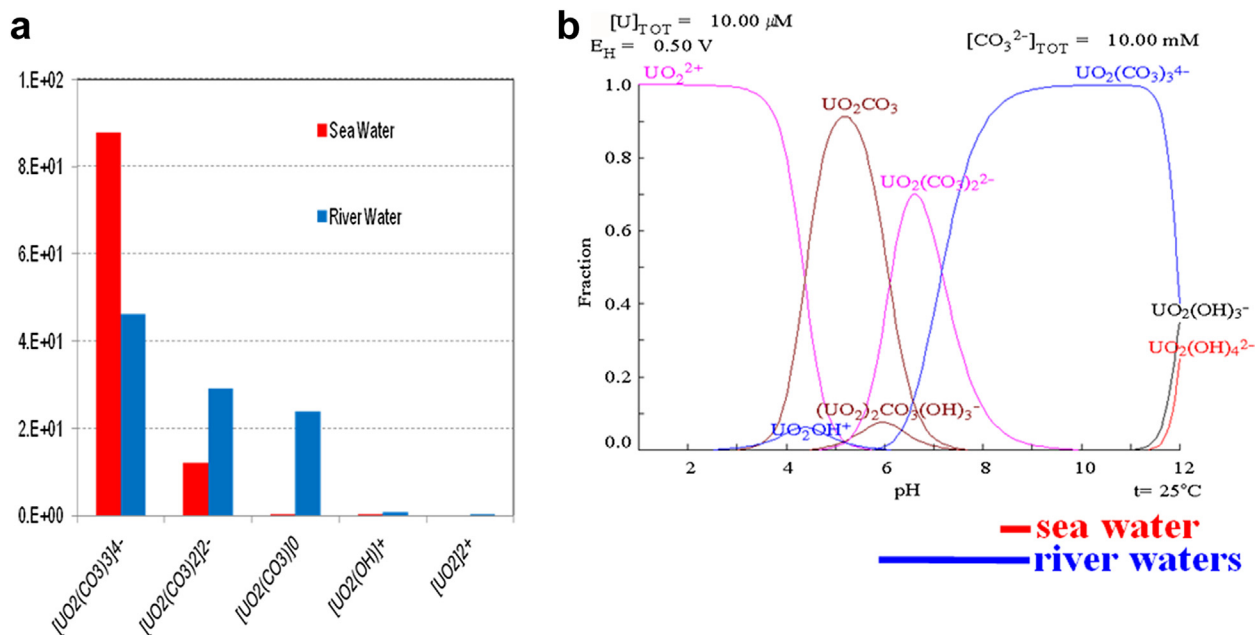
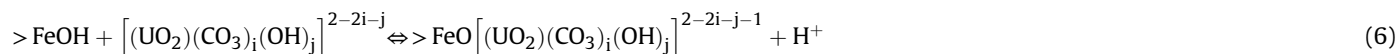


Fig. 3. **a.** Comparison of the uranium species fractions (%) in sea (red) and Amazon River (blue) waters (data from Tables 1b and 2b). **b.** Plot of the fractions of uranyl species as a function of pH. Domains of pH for sea water (red) and water from largest rivers (blue) are noted. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

The surface complex stability constant is then:

scavenging and sedimentation in estuary. The remaining soluble fraction of U is then reduced from the particulate fraction prior to

$$K_{(s,i,j)} = \left[> \text{FeO} \left[(\text{UO}_2)(\text{CO}_3)_i(\text{OH})_j \right]^{2-2i-j-1} \right] \left[\text{H}^+ \right] \left[> \text{FeOH} \right]^{-1} \left[\left[(\text{UO}_2)(\text{CO}_3)_i(\text{OH})_j \right]^{2-2i-j} \right]^{-1} \quad (7)$$

feeding the sea.

In the sea water uranium exists as soluble and as its fraction associated to particulates is restricted the uranium amount that undergoes scavenging is rather small.

Sorption coefficient equation as derived from Degueldre et al. (1994), is then:

$$K_d = \frac{\left\{ K_{(s;0,0)} + \sum_i K_{(s;i,0)} \beta_{(i,0)} \left[\text{H}^+ \right]^{-i} + \sum_i K_{(s;0,j)} \beta_{(0,j)} \left[\text{CO}_3^{2-} \right]^{-j} + \sum_i K_{(s;i,j)} \beta_{(i,j)} \left[\text{CO}_3^{2-} \right]^{-j} \left[\text{H}^+ \right]^{-i} \right\} \left[> \text{SOH} \right]}{\left\{ 1 + \sum_i \beta_{(i,0)} \left[\text{H}^+ \right]^{-i} + \sum_j \beta_{(0,j)} \left[\text{CO}_3^{2-} \right]^{-j} + \sum_{ij} \beta_{(i,j)} \left[\text{CO}_3^{2-} \right]^{-j} \left[\text{H}^+ \right]^{-i} \right\} \left[\text{H}^+ \right] \left[\text{col} \right]} \quad (8)$$

With $K_d = k_{\text{sor}}/k_{\text{des}}$ (kinetic constant for sorption/desorption). These relationships are, however, only valid in the case of reversible sorption. This is not the case any more when sorption turns irreversible by condensation between two colloids (col) in the form of (col₁)-U-(col₂) or when surface precipitation takes place (e.g. carbonate coprecipitation) in which case the approach must be redefined. Reaction (6) could be completed by neutralization of the produced proton with one hydroxyl group; this generally is an exothermal reaction (e.g. Zalts et al., 2008) that is favored at low temperature.

2.2.1. Sorption of uranium on particles in sea water

The association behaviour of uranium on the particulate phase could be driven by sorption (described by surface complexation), surface precipitation or coprecipitation. Because of the low concentration of U, sorption is the most relevant process when calcite does not precipitate.

The sorption model predicts for pH 8 and for the composition of the sea water reduced values due to the presence of the tri-carbonate complex (more than 85% (non-sorbing) while the bi- and mono-carbonate totalize about 10% (sorbing) only). The K_d values are consequently anticipated to be relatively weak.

2.2.2. Sorption of uranium on particles in river water

In the Amazon and non-basic river waters for pH values of the order of 7 the sorption model predicts that some more significant fractions of U are able to associate with the colloid particle phases since the presence of the tri-carbonate complex (<45%) is reduced compared to the bi- or mono-carbonate complexes (>50%). These last complexes contribute to the potential of sorption on iron oxyhydroxide coatings onto inorganic, organic and bioorganic particles.

2.2.3. Comparing the sorption of uranium on particles in sea and river waters

A steady state is suggested: input from rivers is biased by an output due to sorption of U onto particles coupled with their

Experimental work on the sorption coefficient of elements on particle in river and sea water was reported in the 80's. Li (1981) found $\log C_{\text{op}}/C_{\text{sw}}$ (with C_{op} concentration of an element on oceanic pelagic clay sediment and C_{sw} in sea water; a ratio similar to K_d corrected by the particle concentration) values of uranyl of 2–3 in sea water and around 5 in Amazon River water $\log C_p/C_r$ (with C_p concentration of an element on river water particle and C_r in river water) see Fig. 4a. The uranium associated fraction onto colloids and particles may be estimated on the basis of surface complexation and compared to specific experimental data such as those reported earlier e.g. by Li 1981. Model surface complexation data are estimated for pH 8 using a sorption model first described by Degueldre et al. (1994). They show that the sorption may be reduced by ligands such as bicarbonate for a trivalent actinide (see Fig. 4b). The fraction of U on the particle/colloid phase may be estimated on the basis of the particle concentration in the water. For deep ocean water where the redox may locally become reductive, the redox correction may be applied in the sorption model such as reported for actinides e.g. Degueldre (1995), Alonso and Degueldre (2003), Degueldre and Bolek (2009). This behaviour remains local, however, and as a consequence of the reduction of U(VI) in U(IV), the K_d (or $C_{\text{op}}/C_{\text{sw}}$) should increase. The equilibrium is broken by aggregation and sedimentation towards the sea floor. Scavenging reduces the uranium and metal concentrations in sea water (Santschi and Honeyman, 1991). Evaluation of the flux is now possible if the sorption on colloidal particles coupled with their aggregation becomes irreversible.

2.3. Uranium and elements balance in sea water

The element balance in sea water may be modeled and estimated considering the mass of elements and sea water, the input flux of elements (inflow) from river (surface/subsurface) and the inflow flux (desorption, leaching, weathering) from sea waters, balanced by the output flux (formation of evaporates, burial in pore water sediments, sedimentation due to scavenging and precipitation, hydrothermal reactions) of material discarded on the sea floor, while sea water is evaporating concentrating soluble elements in the sea. The mass of water evaporated is recycled after raining as

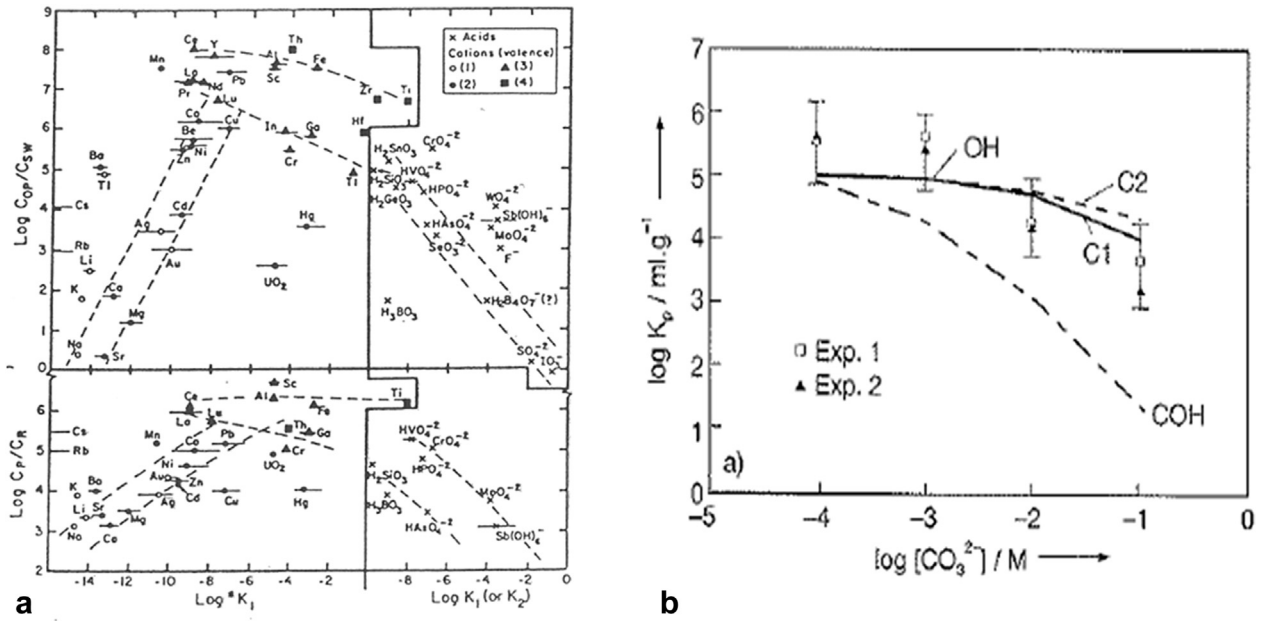


Fig. 4. a: Sorption data of elements on particles in sea water (SW) and Amazon River (R) water (Li, 1981). b: Sorption of An^{3+} at pH 8 as function of carbonate concentration on dirty particulates (Degueldre et al., 1993).

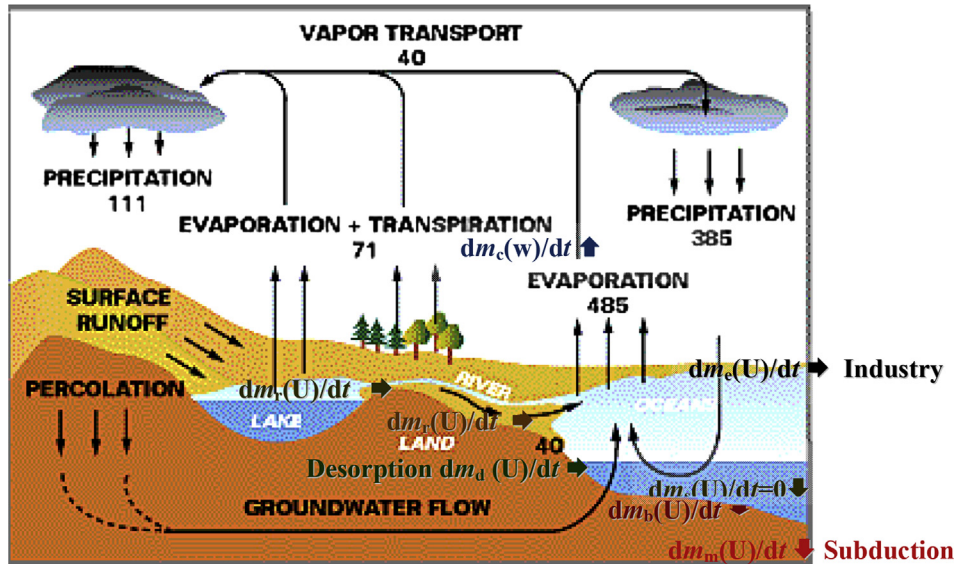


Fig. 5. Phenomena considered for the water and element cycle including input: $dm_r(U)/dt$ from rivers, $dm_d(U)/dt$ from desorption/leaching, outputs from scavenging: $dm_b(U)/dt$, from subduction: $dm_m(U)/dt$, from industry (extraction) $dm_e(U)/dt$. R. Robarts, R. Wetzel, *The Global Water and Nitrogen Cycles*, *SIL News*, 29 (2000) 1–3. There are 4 major pathways of cycling in the global water cycle: precipitation, evaporation, vapor transfer from ocean to land, and return flow in rivers and groundwaters from land to oceans. The following gives the flux of these different pathways: 1. Total precipitation = $0.5 \times 10^6 \text{ km}^3/\text{year}$ (-0.385 over oceans, 0.111 over land). 2. Evaporation from ocean = $0.425 \times 10^6 \text{ km}^3/\text{year}$. 3. Ocean Residence Time, $R_t = (1350 \times 10^6 \text{ km}^3)/(0.425 \times 10^6 \text{ km}^3/\text{yr}) = 3176$ years. 4. Atmospheric water residence time (As part of your learning about the water cycle, please take a moment to calculate the atmospheric water residence time.)

| | |
|---|--|
| $m_r(w)$: mass of water in rivers | $m_s(U)$: mass of uranium in sea water |
| $m_c(w)$: mass of water in clouds | $m_r(U)$: mass of uranium in river waters |
| $m_s(w)$: mass of water in seas | $m_b(U)$: mass of uranium on sea bottom |
| $m_m(w)$: mass of water subducted in magma | $m_m(U)$: mass of uranium subducted in magma |
| | $m_e(U)$: mass of uranium extracted |
| $m_r(U)/m_r(w)$: U concentration in rivers | $m_s(U)/m_s(w)$: U concentration in sea water |

water in river; the fraction breaking through the geo-sphere reappearing eventually in the rivers (surface flows) or in the

(sub-surface flows) as described by Robarts and Wetzel, 2000 (see Fig. 5).

| | |
|---|--|
| $dm_s(U)/dt = 0$ | U amount in equilibrium in sea water |
| $dm_s(W)/dt = 0$ | Water in equilibrium in sea water |
| $\{d[m_s(U)/m_s(W)]/dt = 0\}t \rightarrow t_\infty$ | U concentration at equilibrium in sea water |
| $dm_r(U)/dt = dm_b(U)/dt$ | Input U flux (F_{Imp}) and output U flux (F_{Out}) |
| $dm_r(W)/dt = dm_c(W)/dt$ | Water cycle |
| $dm_e(U)/dt < dm_r(U)/dt$ | U extraction flux (F_{Ext}) |

The four major pathways of cycling in the global water cycle: **precipitation, evaporation, vapor transfer** from ocean to land, and **return flow** in rivers and groundwaters from land to ocean are limited by the following flux:

Total evaporation $496 \times 10^3 \text{ km}^3 \text{ a}^{-1}$ ($425 \times 10^3 \text{ km}^3 \text{ a}^{-1}$ from ocean, $71 \times 10^3 \text{ km}^3 \text{ a}^{-1}$ from land) = total precipitation $496 \times 10^3 \text{ km}^3 \text{ a}^{-1}$ ($385 \times 10^3 \text{ km}^3 \text{ a}^{-1}$ over ocean, $111 \times 10^3 \text{ km}^3 \text{ a}^{-1}$ over land)
 Water transport as vapor $40 \times 10^3 \text{ km}^3 \text{ a}^{-1}$ from above the ocean to above land = Total water flow $40 \times 10^3 \text{ km}^3 \text{ a}^{-1}$ from land to ocean via rivers or underground

The discarded (scavenging, precipitation) element amount on the sea floor may be due to element scavenging by association on colloidal particle, aggregation and sedimentation or by sorption on the sea floor directly, the latter being kinetically slower than the first. Phenomena like subduction in magma (m) and precipitation (pr) are supposed to be restricted compared to scavenging, these restrictions are justified in section 2.4. The phenomena are depicted in Fig. 5 together with a suggested industrial extraction.

Fig. 5 Phenomena considered for the water (W) cycle (adapted from Robarts and Wetzel, 2000) and element (U) cycle including input: $dm_r(U)/dt$ from rivers, $dm_d(U)/dt$ from desorption/leaching, outputs from scavenging: $dm_b(U)/dt$, from subduction: $dm_m(U)/dt$, from industry (extraction) $dm_e(U)/dt$. Fluxes values in $10^3 \text{ km}^3 \text{ a}^{-1}$.

The considered parameters (for U or element X) are listed below:

The equations describing the system and the equilibrium are listed below

Note that subduction and desorption terms may be required to complete the equations, although these correction terms are anticipated to be very small (U subduction and U desorption fluxes negligible). It must also be added that element cycles interact and

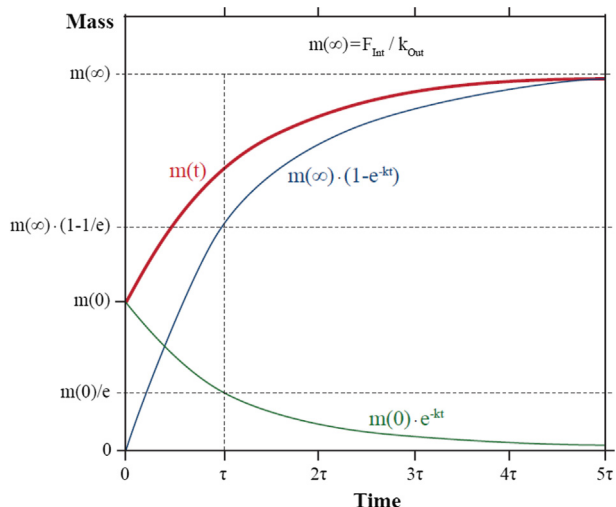


Fig. 6. Evolution of species mass with time in a box model with first-order loss. Adapted from Jacob 1999.

that they should not be studied in isolation (Ref. Robarts and Wetzel, 2000).

2.3.1. Element output from sea water

The output fluxes are needed to describe the system that may be simplified as a one-box model.

The lifetime, τ , of X (or U) in the box is defined as the average time that X remains in the box, that is, the ratio of the mass m (kg) of X in the box to the removal rate F_{Out} (kg s^{-1}):

$$\tau_{Out} = m/F_{Out} \quad (9)$$

The lifetime is also called the residence time. The relative importance of different sinks contributing to the overall removal of a species may be quantified (the sum of all removal rates scavenging, precipitation, coprecipitation and subduction).

The sinks are often first-order, meaning that they are proportional to the mass inside the box. In this case, the lifetime is independent of the inventory of X in the box. Considering a first-order chemical loss for X with rate constant k_{Out} the chemical loss rate is

$$F_{Out} = k_{Out} m \text{ so that } \tau_{Out} \text{ is simply the inverse of the rate constant:}$$

$$\tau_{Out} = M/F_{Out} = 1/k_{Out} \quad (10)$$

The notion of chemical rate constants can be generalized to define rate constants for loss by export ($k_{Out} = 1/\tau_{Out}$). Quantification of U or X in the box may be quantified by $m(t)$ using the depletion equation:

$$m(t) = m(0) e^{(-k_{Out}t)} \quad (11)$$

The model may be completed considering the fraction of suspended matter in sea water $m_s(SM)$ i.e. 20–200 mg kg^{-1} (Lam et al., 2015). The rate constant may then be substituted by $k_{Out} = k_{Out} m_s(SM)$.

The output flux or the scavenged matter may then be fully quantified as depicted in Fig. 6. Subduction in mantle (m) and precipitation (pr) are supposed to be restricted compared to scavenging (Section 2.4).

2.3.2. Element input in sea water

The input fluxes are needed to describe the system as a one-box model.

Uranium (or an element X) inputs in sea water is due to input from surface waters (rivers), shallow and deep waters (underground rivers), sea water contacts with mantle and desorption from the sea bed.

The river input is mainly the sum of all soluble U species. The U associated to particle-colloid is supposed to be eliminated by sedimentation in the estuaries where the non-saline suspension depletes in contact with sea water, the salt acting as cement between particles.

The gain of element (e.g. $m_r(U)$) must be equal to the source input and

$$F_{Imp}(U) = dm_r(U)/dt. \quad (12)$$

This mass balance equation can be solved if the flux is known. The concentration of dissolved uranium has been determined in over 250 river waters from the Orinoco, Amazon, and Ganges basins by Palmer and Edmond (1993). Uranium concentrations are largely determined by dissolution of limestones, although weathering of black shales represents an important additional source in some basins. In shield terrains the level of dissolved U is transport limited. Data from the Amazon indicate that floodplains do not

represent a significant source of U in river waters. In addition, the dissolved U levels in forty rivers from around the world have been determined and these data were coupled with previous measurements to obtain an estimate for the global flux of dissolved U to the oceans. The average concentration of U in river waters is 1.3 nmol kg^{-1} , but this value is biased by very high levels observed in the Ganges-Brahmaputra and Yellow rivers. When these river systems are excluded, the global average falls to $0.78 \text{ nmol kg}^{-1}$ ($0.2 \times 10^{-6} \text{ g l}^{-1}$ or 0.2 ppb). The global U flux from rivers lies in the range of $3\text{--}6 \times 10^7 \text{ mol a}^{-1}$ or about 10 kt a^{-1} . The major uncertainty that restricts the accuracy of this estimate (and that of all other dissolved river borne fluxes) is the difficulty in obtaining representative samples from rivers which show large seasonal and annual variations in runoff and dissolved load. The values extracted from Palmer and Edmond (1993) are more realistic than that used by Cohen (1984): 1 ppb.

The other inputs such as deep waters (underground rivers), sea water contacts with mantle and desorption from the sea bed are discussed in Section 2.4.

The input data may be used for quantification of $m_s(\text{U})(t)$ in Fig. 6.

2.3.3. Combining element (uranium) input and output in sea water

By mass balance, the change with time in the abundance of a species X inside the box must be equal to the difference between sources and sinks:

$$dm_s(\text{U})/dt = F_{\text{Inp}} - F_{\text{Out}} \quad (13)$$

This mass balance equation can be solved for $m(t)$ if all terms on the right-hand-side are known. The solution here may be carried out considering the sinks are first-order in m and the sources are independent of m . The overall loss rate of X is $F_{\text{Out}} = k_{\text{Out}} m$ (Eq. (10)) and an overall source rate F_{Inp} may be defined. Substituting into Eq. (13) gives:

$$dm_s(\text{U})/dt = F_{\text{Inp}} - k_{\text{Out}}m_s(\text{U}) \quad (14)$$

Eq. (14) is readily solved by separation of variables. Integrating both sides over the time interval $[0, t]$, the equation gives by rearrangement,

$$m(t) = m(0) e^{(-k_{\text{Out}}t)} + (F_{\text{Inp}}/k_{\text{Out}})(1 - e^{(-k_{\text{Out}}t)}) \quad (15)$$

A plot of $m(t)$ as given by Eq. (15) is shown in Fig. 6. Eventually $m(t)$ approaches a steady-state value $m^* = S/k$ defined by a balance between sources and sinks ($dm/dt = 0$ in Eq. (13)). Notice that the first term on the right-hand-side of Eq. (15) characterizes the decay of the initial condition, while the second term represents the

approach to steady state. At time $t = 1/k$, the first term has decayed to $1/e = 37\%$ of its initial value while the second term has increased to $(1-1/e) = 63\%$ of its final value.

2.4. Discussion of the box model use

The steady-state assumption allows considerable simplification by reducing differential equations. As should be apparent from the above analysis, one can assume steady state for a species as long as its production rate and its lifetime τ have both remained approximately constant for a time period much longer than τ . When the production rate and τ both vary but on time scales longer than τ , the steady-state assumption is still applicable even though the concentration of the species keeps changing; such a situation is called quasi steady state or dynamic equilibrium. The way to understand steady state in this situation is to appreciate that the loss rate of the species is limited by its production rate, so that production and loss rates remain roughly equal at all times. Even though dm/dt never tends to zero, it is always small relative to the production and loss rates, Ref Jacob 1999.

An upper limit for the age of the oceans is obtained by dividing the amount of an element dissolved in the sea by the amount added each year by rivers. These calculations yield the following figures reported in Table 3. The accumulation or residence time data may be compared with the sorption data for example given by Li (1981) with the trend: the longer the residence time the weaker the sorption on the particles and potentially the larger the concentration (see Fig. 7) or the lower the accumulation time value the stronger the sorption.

The ocean mixing takes place in a secular process driven by shallow flows of warm waters e.g. Gulf Stream followed by pelagic deep flows of cold waters, e.g. along the Antarctica circle inducing mixing in the oceanic systems i.e. Atlantic, Indian, Pacific (ocean mixing pattern). The water mixing time is of the order of 1000 a (Ref. Broecker, 1991).

The subduction of uranium in magma may be estimated on the basis of topographic data. As the result of oceanic lithosphere diving below continental lithosphere, 55,000 km long plates are subject to subduction (Stern, 2002). Over 10^6 a $170\text{--}320 \times 10^9$ t of water would undergo subduction per km of oceanic trench or $170\text{--}320 \times 10^3$ t of water a year and per km (Ref: Kastner et al., 2014). With $m_s(\text{U})/m_s(\text{w})$ 3 ppb ($\mu\text{g kg}^{-1}$) the subducted flux of uranium may be evaluated i.e. ~ 30 t per year. This amount of U (or less since part of the water is under the form of hydrated mineral) should be discarded by the “conveyor belts” trough the trenches. This later value could be corrected from any uranium precipitated on the subduction plan by the effect of hot springs along the oceanic spreading ridges before subduction process itself. This uranium subduction flux is negligible compared to the F_{Out} flux of uranium estimated to undergo scavenging on the sea floor escaping from the soluble phase.

The other inputs such as deep waters (underground rivers), sea water contacts with oceanic mantle and desorption from the sea bed may be discussed as follows.

The impact of deep waters (underground rivers), fluxes may be evaluated.

From a total precipitation water recharge of $111 \times 10^3 \text{ km}^3 \text{ a}^{-1}$, $71 \times 10^3 \text{ km}^3 \text{ a}^{-1}$ evaporate by various processes and $40 \times 10^3 \text{ km}^3 \text{ a}^{-1}$ flow towards the sea in the form of surface water and groundwater (see Fig. 5). Palmer & Edmond consider $30 \times 10^3 \text{ km}^3 \text{ a}^{-1}$ surface water (250 rivers) if the rest ($10 \times 10^3 \text{ km}^3 \text{ a}^{-1}$) is ground water, the uranium input may be estimated from an average uranium concentration in groundwaters. Like for surface water the variability of uranium concentration is large depending of the water chemistry. The following values are

Table 3

Residence time of selected elements in sea water and sorption coefficient on aquatic particles. Ref (Residence time) Burton and Wright, 1981; (Concentration) Turekian, 1968; ($\log C_{\text{Op}}/C_{\text{Sw}}$) Li, 1982.

| Element | Residence time (a) | Concentration (M) | $\log C_{\text{Op}}/C_{\text{Sw}}$ (ml g^{-1}) |
|----------|--------------------------------------|---|---|
| Na | 2.60×10^8 | 4.69×10^{-1} | 0.5 |
| Mg | 4.50×10^7 | 5.27×10^{-2} | 1 |
| K | 1.10×10^7 | 1.02×10^{-2} | 1.8 |
| Ag | 2.10×10^6 | 1.85×10^{-11} | 3.5 |
| Au | 5.60×10^5 | 5.00×10^{-14} | 3 |
| U | 5.00×10^5 | 1.34×10^{-8} | 2.5 |
| Sn | 1.00×10^5 | 4.21×10^{-12} | (5.5) |
| Cu | 5.00×10^4 | 2.36×10^{-9} | 6 |
| Pb | 2.00×10^3 | 1.30×10^{-11} | 7.2 |
| Ni | 1.80×10^4 | 8.18×10^{-9} | 5.5 |
| Pb | 2.00×10^3 | 1.30×10^{-11} | 7.2 |

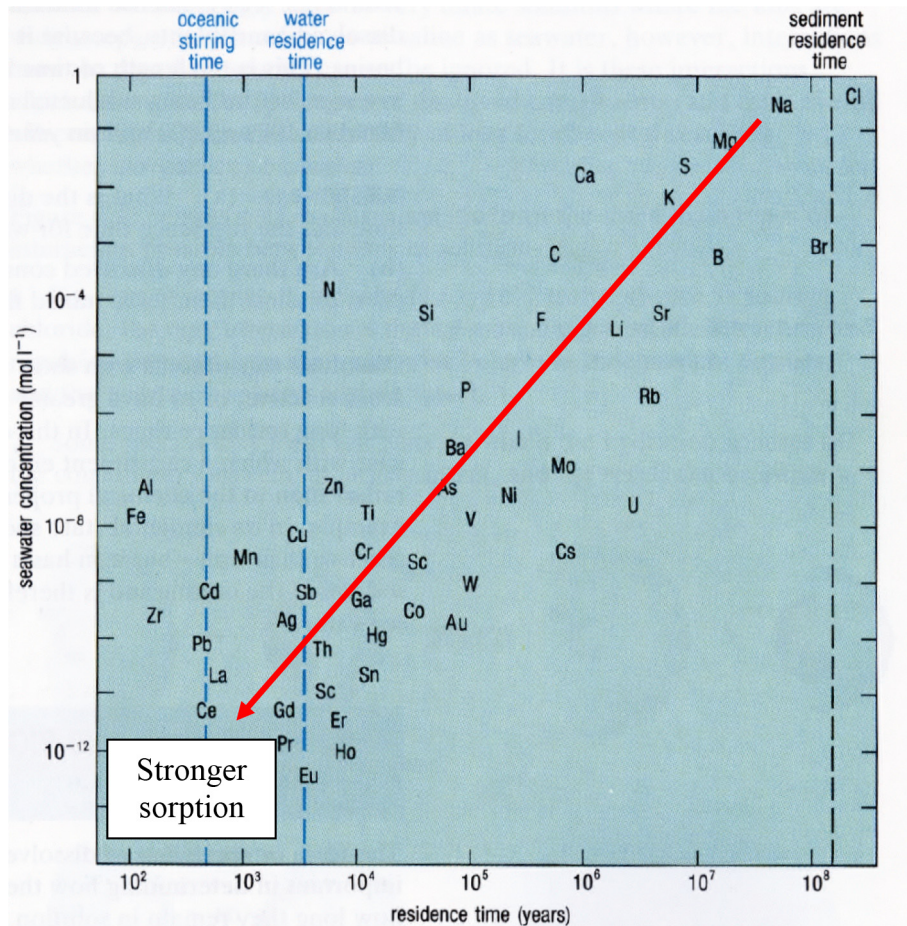


Fig. 7. Concentration and residence time of elements in sea water. As derived from Whitfield (1979).

reported: 1.5–50 ppb for typical waters from South India (Brindha et al., 2011), Uranium concentration in drinking water worldwide (17 countries (regions): Canada, Argentina, Norway, Jordan, Greece, Italy, Kuwait, USA, Greenland (Dk), Turkey, Serbia, Montenegro, Hungary, Germany, Switzerland, India) shows large variations (Bhangare et al., 2013). The uranium in the waters mainly depends upon geochemistry in the area. The water from Jordan had largest range of uranium concentration varying from 0.04 ppb to 1400 ppb. South Greenland had the minimum uranium concentration range of 0.5–1 ppb only. In an other study, comparing groundwaters from Australia, Bangladesh, China, India, Irak, Japan, Pakistan, USA (Tawfiq, 2013) found values from 0.2 ppb to 20 ppm. An average uranium concentration of 10 ppb may be tentatively used. Multiplying the groundwater recharge $10 \times 10^3 \text{ km}^3 \text{ a}^{-1}$ by the suggested average U concentration gives 10 kt a^{-1} , an imprecise value, which would request assessment, but comparable to the input by surface water.

The impact of U release from sea water contacts with oceanic mantle may also be evaluated.

Along the 60,000 km ocean ridges, sea water may locally contacts mantle lavas generating seafloor hydrothermal activity, black smokers and chimneys Ref. Von Damm, 1990. Deep-sea hydrothermal vents are an important source of iron, an element that can limit marine productivity and trap trace elements. Recently Resing et al. (2015) estimated a global hydrothermal dissolved iron input of $3\text{--}4 \text{ Gmol a}^{-1}$ to the ocean interior. Recent studies have questioned the view that most of the iron discharged from such vents is removed from seawater close to its source. The impact of iron in the

aquatic system is relevant since iron may be partially soluble as Fe(II) but can also be suspended and transported locally as smoke of colloidal particles that can latter aggregate and trap elements during sedimentation e.g. Bennett et al. (2008). This influences element cycles in a significant way. The effect on uranium speciation is however limited by the surface complexation as presented in Section 2.2.

The impact of U desorption from the sea bed may finally be evaluated.

The leaching rate may be estimated as follows. The average concentration of U in sea sediments is 3 ppm (Dunk et al., 2002). The total surface of the ocean is $3.6 \times 10^{14} \text{ m}^2$ may be corrected (fractal dimension) by a factor 10^n . The potential leaching of 1 nm sediment per year is postulated (to be compared to the larger sedimentation rate). The sediment leaching rate becomes $3.6 \times 10^{5+n} \text{ m}^3$. The U leaching rate becomes $1 \times 10^n \text{ t}$ of U per year. Actually, for n ranging from 1 to 2, the leaching rate remains much smaller than the U river input rate.

3. Revisiting the nuclear fuel cycle

The nuclear fuel cycle has been revisited extensively in the scientific literature. Starting with classical U mining and coupling the utilization of GenII reactors with GenIV reactors after fuel reprocessing and recycling, Poinssot et al., 2015, target improvement of the overall environmental footprint. For fuel cycle optimization, multiple generation of sodium fast reactor (SFR) may be needed to fulfill full minor actinide (MA) recycling Ref. Lindley et al.,

2015. The analysis has also been extended to the thorium fuel cycle, since closed Th-based fuel cycles are well known to have lower equilibrium radiotoxicity and may provide advantage in resource utilization (Lindley et al., 2015). However the initial resource of fissile remains the key limitation when considering nuclear as a renewable.

Definitions of renewable energy technologies often omit mention to nuclear energy source, with an exception made for the natural nuclear decay heat within the Earth: the geothermal energy. Based on the analysis of the uranium occurrence in sea water it is realistic to suggest that the extraction of uranium from sea water performed with parsimony would upgrade the utilization of the resource. Recommendations are needed considering the front end as well as the fuel utilization and reutilization after reprocessing, and the reactors type from Generation IV and IV + to reach the label “renewable”.

3.1. Front end with uranium extraction from sea water

Unconventional uranium resources include up to 4500 megatons of uranium contained in sea water. In this section the extraction of uranium from sea water using inorganic, organic and bioorganic sorbent is explored.

With inorganics absorbents, little has been carried out maybe because of their strong affinity to sorb dispersed organic matter as well as > FeOH coated colloidal particles limiting their utilization. Among these absorbents hydrous TiO₂ is the most cited, e.g. Kanno, 1984. Most of the R&D has been performed with organic and bioorganic absorbents.

With organic sorbent, amidoxime group functional gel in sea water pH 8.3 is selective for adsorption of uranium by chelation as demonstrated by Tamada et al. (2006). The amidoxime polymer gel absorbent offers high adsorption efficiency as reported by Hara et al., 2016.

In Japan, the technology to extract uranium from sea water has been demonstrated at the laboratory scale, and extraction costs were estimated in the mid-1990s to be ~US\$ 260 per kg of U (Nobukawa et al., 1992) but scaling up laboratory-level production to thousands of tons needs to be proven (WEC, 2007).

One method of extracting uranium from sea water is using a uranium-specific nonwoven fabric as an absorbent. The total amount of uranium recovered in an experiment in 2003 from three collection boxes containing 350 kg of fabric was >1 kg of yellow cake after 240 days of submersion in the ocean (Seko et al., 2003).

In 2006 the same research group demonstrated that if 2 g of U per kg of adsorbent is submerged for 60 days at a time and used 6 times, the uranium cost is calculated to be 88,000 yen (about 880 US\$) per kg of U, including the cost of adsorbent production, uranium collection, and uranium purification. When 6 g of U per kg of adsorbent and 20 repetitions or more becomes possible, the uranium cost reduces to 15,000 yen (about 150 US\$) per kg see Tamada et al., 2006. This price level is equivalent to that of the highest cost of the minable uranium. Today, large scale marine experiments need to be planned for improving the system performance and making the collection of uranium from sea water more economically competitive e.g. Nor Azillah Fatimah et al., 2012.

In 2012, ORNL researchers announced the successful development of a new absorbent material dubbed HiCap that outperforms the previous best adsorbents, which perform surface retention of solid or gas molecules, atoms or ions Ref. Oyola et al., 2013. HiCap also effectively removes toxic metals from water, according to results verified by researchers at Pacific Northwest National Laboratory e.g. Kim et al., 2013. Other absorbing groups have also been tested such as imidedioxime e.g. Rao et al., 2013, or groups derived from carbamoylphosphoramidic acid H₂N–C=O–NH–P=O(OH)₂

e.g. Carboni et al., 2013. Extraction using functional groups such as diazonium R–C(=NOH)–NH–(HON =)C–R grafted on C fiber were tested for their high adsorption efficiency, Ref. Mayes et al., 2013.

Among the other methods to recover uranium from sea water, one seems promising: algae bloom to concentrate uranium (Heide et al., 1973).

The deployment of the uranium extraction system has been sketched by Schneider et al. (2013). The extraction should be carried out using braid absorbent, mooring the system over months. The ecological impact of the marine environment (plankton, fish eggs) is restricted by the frequency of extraction. The extraction of other metals would take place. Elution and absorbent reutilization would reduce costs. Both cost analysis and energy assessment would be foreseen.

So far, no more than a very small amount of uranium has been recovered from sea water in a laboratory (WEC, 2007). Several organisations, including Japan's Atomic Energy Agency, ORNL, USA and the Bhabha Atomic Research Centre in India, are attempting to perform extraction. Their methods include the use of strips of ion-exchanging plastic, braided with polystyrene to toughen them up. These are placed in wire cages and anchored in a current of sea water. After a month or two, the plastic is removed and soaked in acid to dissolve the uranyl tri-carbonate. The solution is then treated to precipitate uranium oxide.

Another alternative method to recover uranium from sea water, nano-membrane filtering (Cooper et al., 2003) is also promising. It could be coupled in the process of sea water desalination use of membranes.

According to the OECD, uranium may be extracted from sea water using Seko et al., 2003, method for about ~US\$ 300 per kg of U (OECD, 2008). At the moment, the uranium extraction from sea costs e.g. (290 \$ per kg U) about two times as much as conventional mining (100–200 \$ per kg U), but some countries might regard that as a small price to pay for security of supply (Schneider et al., 2013). Absorbent recycling and production of other strategic metals may compensate the costs. Cost reduction may also become effective using pelagic stream, high tide on specific location and hot water.

3.2. Impact on the fuel cycle

Extraction of uranium from solid ores with wt% U level even if economically effective today has limited potential. Extraction of uranium from other ores at the ppm level (phosphate, coal) may extend the potential toward unconventional resource. The reprocessing and recycling of uranium and other actinides offers interesting options. Specific industrial residues e.g. desalination of water may reveal sources of uranium that may be exploited. Even if this approach may be qualified to be sustainable it is not proven to be renewable.

Extractions from fluids with ppb U level (i.e. sea water) have a large potential. River waters below the ppb U level have the advantage of flow but the disadvantage of lower concentrations. In the front end extraction of uranium from sea water may be coupled with the extraction of other metals. A comparison of the U resources from ores, phosphates, coals and sea waters is sketched in Fig. 8. The resource is compared with the annual production rate. The production rate is compared for the present ore extraction, the potential uranium extraction from phosphates and coal, and one tenth of the fluvial U input in the sea. This latter condition would make the uranium extraction from the sea renewable. This concept would complete the conventional definition of renewable energy generally defined as: energy that comes from resources which are naturally replenished on a human timescale such as sunlight, wind, rain, tides, waves, and geothermal heat e.g. Ellabban et al., 2014. The ecological aspects of this extraction compared to solid rock mining

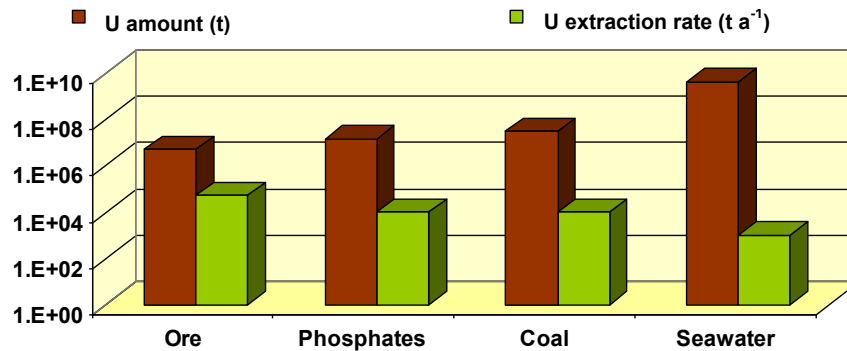


Fig. 8. Comparison of the resource amount of uranium from various sources together with the extraction rate (for ore ($\sim 7 \times 10^4 \text{ t a}^{-1}$), phosphate (potentially $5 \times 10^3 \text{ t a}^{-1}$) and coal (potentially $5 \times 10^3 \text{ t a}^{-1}$) and as required from sea to reach the renewable status). Data as discussed in introduction chapter and as required for sea water to reach the label renewable ($\sim 10^3$ (or less) t a^{-1} , see Section 2.3 and 3).

with the tailings concerns make the extraction from the sea very attractive.

Uranium resource is not likely to be an issue until 2050–2100 (Rooney et al., 2015). Any unexpected fall in uranium mine capacity of 5000 t per year or more could have a significant effect on the price. Speed of U mine capacity may be masked by the source diversification while in situ leaching e.g. Kazakhstan, may modify the speed of market supply.

However, with today's fuel utilization in LWRs 4 to 7 Mt of U should be consumed until 2050 (Gabriel et al., 2013). The U recovery from sea water would guarantee a large resource. With the molten salt reactor (MSR) the uranium consumption would be reduced a factor ~ 10 which would also ameliorate the utilization of the fissile resources.

Options for fissile resources are also suggested with actinide utilization as fuel component within multi-recycling strategy e.g. Lindley et al. (2015).

The efficiency of energy conversion is a key issue to reduce fuel consumption for a maximum of energy production. Clearly the GenIV reactors: the very high temperature reactor (VHTR), the SFR, the super critical water reactor (SCWR), the gas fast reactor (GFR), lead-cooled fast reactor LFR and the MRS, are more efficient than the GenII light and heavy water reactors (LWR, HWR) because among their advantages (e.g. Locatelli et al., 2013; Orlander, 2009; Abram and Ion, 2008) the GenIV operational coolant temperature is higher than the GenII and the yield of energy conversion via thermodynamic cycle better. In addition, the fast GenIV reactors (SFR, GCR, LFR, MSFR) are actually more efficient than the thermal (VHTR, SCWR, MSThR) for neutronic reason: the fast reactor can burn ^{238}U while the thermal not. Finally recent reconsiderations of the liquid fuel reactors (MSThR and MSFR (GenIV+)) make them attractive because they are considered as the most sustainable of the 6 GenIV reactors (Serp et al., 2014) and because part of the fission products e.g. Xe, Kr and other volatiles are discarded from the molten salt fuel during operation. This makes the neutronic more attractive, some of the these fission products (e.g. Xe) being strong neutron absorbers (reducing the neutron flux). This process allows consequently a better fuel utilization decreasing the neutron lost by absorption in stead of fission.

Consequently, options for more efficient reactors Gen IV & IV + such as molten salt reactors (MSR) (Th: thermal or F: fast) or fast reactors (FR) may be suggested to improve neutronics compared to the LWR to fulfill the renewable concept requirements i.e. with an uranium consumption below 1 kt a^{-1} and with a world reactor park of 500 units. This would imply research for reducing the consumption following the guide line:

- With a consumption rate of $\sim 200 \text{ t U/GW}$ an electrical for LWR (AIEA, 2012) it shall not be possible.
- With a MSThR consumption rate of $\sim 20 \text{ t U/1 GW a}$ (Engel et al., 1980) becomes possible
- With the FR a consumption rate of $\sim 2 \text{ t U/1 GW a}$ (e.g. Cohen, 1983) would be reached. Finally,
- With the MSFR consumption rate of $\sim 0.8 \text{ t U/1 GW}$ an electrical should become possible (Leblanc, 2015).

The deployment of FR or MSFR would better rationalize the uranium consumption (Gao and Ko, 2014) and makes U utilization more sustainable say renewable if the world consumption of U is maintained below 10 kt a^{-1} say 1 kt a^{-1} (10% the annual input from rivers since the uncertainty on the input rate value is larger e.g. non including underground waters input, see section 2.4) and its extraction carried from the sea. In this context the concentration of uranium in the sea water would pass from 3.3 ppb to 3 ppb over a period of 5 residence times (e.g. 2 Ma). Under these conditions the uranium extraction from sea water could be carried in a renewable way its concentration remaining quasi constant over time.

4. Conclusion

Uranium extraction is the first step of the nuclear fuel cycle. In today's practice the only extractions are carried out on solid ores such as uranium rich minerals (% level, total mass 5.2 Mt, with an extraction rate of $\sim 7 \times 10^4 \text{ t a}^{-1}$, or minerals such as phosphates (ppm level, total mass 15 Mt). For some years extraction of uranium from sea water (ppb level, total mass 4.5 Gt) has been the topic of investigations, especially in Japan due to national interest. With the huge oceanic volume to treat during practical extraction the amount of uranium from sea water would remain quasi constant. This study demonstrates that for potential commercial extraction the pick-up part could be balanced by the input of the uranium soluble fraction as estimated from the river income ($\sim 10 \text{ kt a}^{-1}$). This work shows that with low uranium consumption and an extraction with parsimony from sea water could be carried in a renewable way if its concentration remains quasi constant. Recommendations for optimal conversion (reactor science research) and extraction from the sea with use of specific gel panels or absorbent fabric (processing research) in high tide environments or oceanic current pelagic area are suggested. It would also be suggested to proceed to more environmental science research to better quantify the uranium input - output equilibrium in the oceans at the level of our planet.

Acknowledgements

This multidisciplinary literature review paper has been supported by several specific discussions with expert in various fields. Acknowledgements are due to with Pr Dr Kazuhiro Hara, University of Kyushu for the exchange of documents on uranium extraction, Dr Tony Williams, Axpo, Switzerland for his advice on the uranium market and PD Dr Wolfgang Hummel for his remarks on uranium speciation. Thanks are also due to Dr Stefan Hirschberg for his suggestions. An anonym reviewer must also be acknowledged constructive comments.

References

- Abram, T., Ion, S., 2008. Generation-IV nuclear power: a review of the state of the science. *Energy Policy* 36, 4323–4330.
- AIEA, 2012. <https://infocis.iaea.org/NFCSS/NFCSSMain.asp?RightP=Calculation&EPage=2>.
- Alonso, U., Degueldre, C., 2003. Modelling americium sorption onto colloids: effect of redox potential. *Colloids Surf. A* 217, 55–62.
- Ball, J.W., Nordstrom, D.K., 1992. User's Manual for WATEQ4F, with Revised Thermodynamic Data Base and Test Cases for Calculating Speciation of Major, Trace, and Redox Elements in Natural Waters. U.S. Geological Survey Open-File Report 91-183, p. 189.
- Bardi, U., 2010. Extracting minerals from seawater: an energy analysis. *Sustainability* 2, 980–992.
- Bennett, S.A., et al., 2008. The distribution and stabilisation of dissolved Fe in deep-sea hydrothermal plumes. *Earth Planet. Sci. Lett.* 270, 157–167.
- Bhangare, R.C., Tiwari, M., Ajmal, P.Y., Sahu, S.K., Pandit, G.G., 2013. Laser fluorimetric analysis of uranium in water from Vishakhapatnam and estimation of health risk. *Radiat. Prot. Environ.* 36, 128–132.
- Brindha, K., Elango, L., Nair, R.N., 2011. Spatial and temporal variation of uranium in a shallow weathered rock aquifer in southern India. *J. Earth Syst. Sci.* 10, 911–920.
- Broecker, W.S., 1991. The great ocean conveyor. *Oceanography* 4, 79–89.
- Burton, J.D., Wright, D., 1981. Seawater and its evolution. In: Cocks, L.R.M. (Ed.), *The Evolving Earth*. British Museum, London, pp. 89–101.
- Carboni, M., Abney, C.W., Liu, Sh., Lin, W., Li, W., 2013. Highly porous and stable metal-organic frameworks for uranium extraction. *Chem. Sci.* 4, 2396–2402.
- Cohen, B.L., 1983. Breeder reactors: a renewable energy source. *Am. J. Phys.* 51, 75–76.
- Ch. H. Cooper, A. Cummings, M. Starostin, Ch. Honsinger (2003-03-07). Purification of fluids with nanomaterials. World patent WO2004080578 Retrieved 2008-04-22.
- Davister, A., Martin, J., 1989. Improvement and results acquired through six year of industrial uranium extraction from phosphoric acid by the Prayon process, the recovery of uranium from phosphoric acid. IAEA TECDOC 533.
- Degueldre, C., 1995. Retention of redox sensitive elements in aquifers- the case of neptunium. *J. Environ. Radioact.* 29, 75–87.
- Degueldre, C., Bolek, M., 2009. Modelling colloid association with plutonium: the effect of pH and redox potential. *Appl. Geochem.* 24, 310–318.
- Degueldre, C., Ulrich, H.-J., Silby, H., 1994. Sorption of Am onto montmorillonite, illite and hematite colloids. *Radiochim. Acta* 65, 173–179.
- Devereux Carter, M., 1976. The national coal-resources data system of the U.S. geological survey. *Comput. Geosci.* 2, 331–340.
- Djogic, R., Sipos, L., Branica, M., 1986. Characterization of uranium(VI) in seawater. *Limnol. Oceanogr.* 31, 1122–1131.
- Dunk, R.M., Mills, R.A., Jenkins, W.J., 2002. A reevaluation of the oceanic uranium budget for the Holocene. *Chem. Geol.* 190, 45–67.
- Ellabban, O., Abu-Rub, H., Blaabjerg, F., 2014. Renewable energy resources: current status, future prospects and their enabling technology. *Renew. Sustain. Energy Rev.* 39, 748–764.
- I. Emsley, WNA 2013 Fuel Market Report. Proceedings International Symposium on Uranium Raw, Material for the Nuclear Fuel Cycle, IAEA, 23-27, June 2014.
- Engel, J.R., Bauman, H.F., Dearing, J.F., Grimes, W.R., McCoy, H.E., Rhoades, W.A., 1980. Conceptual Design Characteristics of a Denaturated Molten-salt Reactor with Once-through Fueling. ORNL TM7207.
- Frondel, J.W., Fleisher, M., 1950. A Glossary of Uranium and Thorium –bearing Minerals. US Geological Survey, US DOI. Circular, 74.
- Gabriel, S., Baschwitz, A., Mathonnière, G., Fizaine, F., Eleuet, T., 2013. Building future nuclear power fleets: the available uranium resources constraint. *Resour. Policy* 38, 458–469.
- Gaillardet, J., Dupre, B., Allegre, C.J., Négrel, P., 1997. Chemical and physical denudation in the Amazon River basin. *Chem. Geol.* 142, 141–173.
- Gao, F., Ko, W.L., 2014. Modeling and system analysis of fuel cycles for nuclear power sustainability (I): uranium consumption and waste generation. *Ann. Nucl. Energy* 65, 10–23.
- Hara, K., Nishimoto, T., Fujiwara, S., Fujii, T., Hidaka, Y., Okabe, H., 2016. Attempts at capturing ppb-level elements from sea water with hydrogels. *Progr. Nucl. Energy* (in press).
- Heide, E.A., Wagener, K., Paschke, M., Wald, M., 1973. Extraction of uranium from sea water by cultured algae. *Naturwissenschaften* 60, 431.
- Hurst, F.J., 1989. The recovery of uranium from phosphates: current status and trends, the recovery of uranium from phosphoric acid. IAEA TECDOC 533.
- Jacob, D.J., 1999. Introduction to Atmospheric Chemistry. Princeton University Press.
- Kanno, M., 1984. Present status of study on extraction of uranium from sea water. *J. Nucl. Sci. Technol.* 21, 1–9.
- Kastner, M., Solomon, E.A., Harris, R.N., Torres, M.E., 2014. Chapter 4.4.3-Fluid origins, thermal regimes, and fluid and solute fluxes in the forearc of subduction zones. *Dev. Mar. Geol.* 7, 671–733.
- Kim, J., Tsouris, C., Mayes, T.R., Oyola, Y., Saito, T., Janke, J.C., Dai, S., Schneider, E., Sachde, D., 2013. Recovery of uranium from seawater: a review of current status and future research needs. *Sep. Sci. Technol.* 48, 367–387.
- Lam, Ph.J., Twining, B.S., Jeandel, C., Roychoudhury, A., Resing, J., Santschi, P., Anderson, R., 2015. Methods for analyzing the concentration and speciation of major and trace elements in marine particles. *Prog. Oceanogr.* 133, 32–42.
- Leblanc, D., 2015. Terrestrial Energy, Personal Communication.
- Li, Y.-H., 1981. Ultimate removal mechanisms of elements from the ocean. *Geochim. Cosmochim. Acta* 45, 1659–1664.
- Li, Y.-H., 1982. Ultimate removal mechanisms of elements from the ocean (reply to a comment by M.W. Whitfield and D.R. Turner). *Geochim. Cosmochim. Acta* 46, 1993–1995.
- Lindley, B.A., Fiorina, C., Gregg, R., Franceschini, F., Parks, G.T., November 2015. The effectiveness of full actinide recycle as a nuclear waste management strategy when implemented over a limited timeframe – Part I: uranium fuel cycle. *Progr. Nuclear Energy* 85, 498–510.
- Locatelli, G., Mancini, M., Todeschini, N., 2013. Generation IV nuclear reactors: current status and future prospects. *Energy Policy* 61, 1503–1520.
- Maloubier, M., Solari, P.L., Moisy, Ph., Monfort, M., Den Auwer, Ch., Moulin, Ch., 2015. XAS and TR-LIF spectroscopy of uranium and neptunium in seawater. *Dalton Trans.* 44, 5417–5427.
- Maslov, O.D., Tserenpil, Sh., Norov, N., Gustova, M.V., Filipov, M.F., Belov, A.G., Altangerel, M., Enhat, N., 2010. Uranium recovery from coal ash dumps of Mongolia. *Solid Fuel Chem.* 44, 433–438.
- Mayes, R., Sun, X.-G., Dai, Sh., Brown, S., Gorka, J., Yue, Y., 2013. Advanced Nanosynthesis Absorbents. *Progr. Rev. Document DOE NE: Fuel resources, Uranium from seawater program*.
- Millero, F.J., 2013. *Chemical Oceanography*. CRC Press.
- Nikanorov, A.M., Brazhnikova, L.V., 2002. Water chemical composition of rivers, lakes and wetlands. *Encycl. Life Support Syst.* 2, 1–39.
- Nininger, R.D., 1954. The Uranium Ore Minerals, from Minerals for Atomic Energy. D. Van Nostrand Company Inc., NY.
- Nobukawa, H., Michimoto, J., Kobayashi, M., Nakagawa, H., Sakakibara, J., Takagi, N., Tamehiro, M., 1992. Development of a floating type system for uranium extraction from sea water using sea current and wave power. *J. Schip Build. Soc. Jpn.* 168, 321–325.
- Nor Azillah Fatimah, O., Jamaliah, Sh., Siti Fatahiyah, M., 2012. A review of uranium extraction from seawater: recent international research and development. *INIS Collect.* 44 (4).
- OECD, March 2008. Uranium Resources 2003: Resources, Production and Demand. OECD World Nuclear Agency and International Atomic Energy Agency, p. 22. Retrieved 2008-04-23.
- OECD NEA & IAEA, 2011. Uranium 2011: Resources, Production and Demand (“Red Book”).
- OECD NEA & IAEA, 2014. Uranium 2014: Resources, Production and Demand (“Red Book”).
- Orlander, D., 2009. Nuclear fuels – present and future. *J. Nucl. Mater.* 389, 1–22.
- Oyola, Y., Sato, T., Brown, S., Dai, Sh., Janke, Ch.J., 2013. Advanced Absorbent Development Employing Radiation-induced Graft Polymerisation. *Progr. Rev. Document DOE NE: Fuel resources, Uranium from seawater program*.
- Palmer, M.R., Edmond, J.M., 1993. Uranium in river water. *Geochim. Cosmochim. Acta* 57, 4947–4955.
- Prat, O., Vercouter, Th., Ansoborlo, E., Fichet, P., Perret, P., Kurtio, P., Salonen, L., 2009. The uranium speciation in drinking water from drilled wells in Southern Finland and its potential links to health effects. *Environm. Sci. Technol.* 43, 3941–3946.
- Poinsot, Ch., Bourg, S., Boullis, B., Improving the nuclear energy sustainability by decreasing its environmental footprint. Guidelines from life cycle assessment simulations. *Progr. Nuclear Energy*, (in press), Corrected Proof, Available online 27 November 2015.
- Rao, L., Tian, G., Sun, X., Endriz, F., 2013. Coordination of UO_2^{2+} with Amidoxime-related Ligands: Thermodynamics, Kinetics and Structure. *Progr. Rev. Document DOE NE: Fuel resources, Uranium from seawater program*.
- Resing, J.A., Sedwick, P.N., German, Ch. R., Jenkins, W.J., Moffett Bettina, J.W., Sohst, M., Tagliabue, A., 2015. Basin-scale transport of hydrothermally dissolved metals across the South Pacific Ocean. *Nature* 523, 200–203.
- Roberts, R., Wetzel, R., 2000. The Global Water and Nitrogen Cycles, 29. *SIL News*, pp. 1–3.
- Rooney, M., Nuttall, W.J., Kazantzis, N., 2015. A dynamic model of the global uranium market and nuclear fuel cycle. *Resour. Policy* 43, 50–60.
- Saito, K., Miyauchi, T., 1982. Chemical forms of uranium in artificial seawater. *J. Nucl. Sci. Technol.* 19, 145–150.
- Santschi, P.H., Honeyman, B.D., 1991. Are Scavenging and Particle Fluxes in the Ocean Regulated by Coagulation? Radionuclides in the Study of Marine Processes. Springer, pp. 107–115.

- Schneider, E., Linder, H., Schade, D.J., 2013. Cost and Energy Assessment. Progr. Rev. Document DOE NE: Fuel resources, Uranium from seawater program.
- Seko, N., Katakai, A., Hasegawa, Sh., Tamada, M., Kasai, N., Takeda, H., Sugo, T., Saito, K., 2003. Aquaculture of uranium in seawater by a fabric-adsorbent submerged system. Nucl. Technol. 144, 274–275.
- Serp, J., Allibert, M., Beneš, O., Delpech, S., Feynberg, O., Ghetta, V., Heuer, D., Holcomb, D., Ignatiev, V., Kloosterman, J.L., Luzzi, L., Merle-Lucotte, E., Uhlir, J., Yoshioka, R., Zhimin, D., 2014. The molten salt reactor (MSR) in generation IV: overview and perspectives. Progr. Nucl. Energy 77, 308–319.
- Stern, R.J., 2002. Subduction zones. Rev. Geophys. 40, 1012–1050.
- Tamada, M., Seko, N., Kasai, N., Shimizu, T., 2006. Cost estimation of uranium recovery from seawater with system of braid type adsorbent. in Japanese Nippon. Genshiryoku Gakkai Wabun Ronbunshi. 5, 358–363. translated into English: J. Atomic Energy Society of Japan/Atomic Energy Society of Japan, 5, 2006, 358–363.
- Tawfiq, N.T., 2013. Uranium and radon concentration in ground water in Aucashat city. (Iraq) and the associated health effects. Adv. Appl. Sci. Res. 4, 167–171.
- Turekian, K.K., 1968. Oceans. Prentice-Hall.
- Von Damm, K.L., 1990. Seafloor hydrothermal activity: black smoker chemistry and chimneys. Annu. Rev. Earth Planet. Sci. 18, 173–204.
- WEC, 2007. Survey of Energy Resources 2007 Uranium - Resources. World Energy Council. Retrieved, 2008-05-14.
- Whitfield, M., 1975. An improved specific interaction model for seawater at 25°C and 1 atmosphere total pressure. Mar. Chem. 3, 197–213.
- Whitfield, M., 1979. The mean oceanic residence time (MORT) concept - a rationalisation. Mar. Chem. 8, 101–123.
- Zalts, A., El Hasi, C., Rubio, D., Urena, A., D'Onofrio, A., 2008. Pattern formation driven by an acid-base neutralization reaction in aqueous media by gravitational field. Phys. Rev. E 77, 015304.