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Technetium-99 (Tc) is an anthropogenic radioactive contaminant of significant environmental concern. The total Tc inventory continues to increase world-wide due to generation of the nuclear power, and methods are needed for its remediation. One such approach is reduction of TcO_4^-, the most common chemical form of aerobic Tc, converting it to less-mobile Tc(IV) and utilization of iron minerals as crystalline media for Tc(IV) stabilization. This review article discusses mechanisms of mononuclear substitution of Fe with Tc(IV) and its incorporation of into lattice structure of iron oxides, i.e. predominantly magnetite, which could provide a sustainable platform for Tc immobilization.

Abiotic Reductive Removal and Subsequent Incorporation of Tc(IV) into Iron Oxides: A Frontier Review

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Abstract

This narrow-focused but deeply elaborated review on incorporation mechanisms of Tc-99 radioisotope in iron oxides and oxyhydroxides presents discussion on two main subjects: predominant form of the reduced Tc(IV) oxide in iron oxidation products and Fe(II)/Fe(III) substitution with Tc(IV) in the magnetite lattice. Detailed analysis of the most relevant to abiotic Tc reduction by iron oxides and oxyhydroxides studies is given in support of the first subject, and comparative review of the EXAFS results is presented to scrutinize the mechanism of Tc(IV) incorporation in magnetite. Considering the risks, imposed with environmental mobility of radiological materials, i.e. Tc-99 (highly mobile in aerobic conditions beta emitter), the possibility of sequestration and immobilization of Tc into lattices of iron minerals has been intensively investigated and several discrepancies among different studies exist. This review systematizes main studies conducted on the topic, and addresses limitations of the common premises, i.e. importance of similarities of atomic radii for substitution mechanism, as well as ambiguity of EXAFS interpretations for iron oxides and oxyhydroxides.

1. Introduction

Cation substitution in minerals has been extensively studied over a century as part of fundamental geochemical research on distribution of chemical elements in earth minerals and cosmic matter.[1] Cation dopant substitution acquired also the applied foci, related to enhancement of semiconductors and conductors, and multiferroic properties of materials.[2,3] Moreover, some minerals, i.e. iron oxides, can act as sinks for toxic metals in the environment.[4] Here, we discuss the functionality of the cation substitution as a mechanism for immobilization of overwhelmingly anthropogenic and radioactive element technetium (Tc-99) in iron oxides / oxyhydroxides in industrial environment of nuclear wastes processing.

In trace amounts, Tc occurs in the earth crust (uranium ores); however it is mainly obtained in nuclear reactors with Tc-99 as the dominant isotope in nuclear fuel cycle, yielding up to 6.3% from thermal neutron fission of nuclear fuel.[5] It is a long-lived radioisotope (213,000 years; relatively low specific activity of 17 μCi/mg or 629 MBq/g; weak β^- radiation of 0.29 MeV) with high mobility in its most common in the aerobic conditions oxidation state of VII (pertechnetate anion, TcO_4^-).[5] Reduction of the pertechnetate to the state of IV (Tc dioxide, existing in the hydrated form, $TcO_2{\bullet}nH_2O$) reduces its solubility and mobility and therefore risks associated with its migration in the subsurface.[6,7] Difficulties of such approach related to the inevitable re-oxidation of Tc(IV) to Tc(VII) in the aerobic environment encouraged an array of studies on search and development of a matrix with the immobilizing capabilities preventing Tc(IV) re-oxidation and leakage to the environment. Examples of such studies include, but not limited to, subsurface reduction of technetium with microorganisms;[8,9] heterogeneous reduction at the solid-water interfaces by structural, ion-exchangeable, and edge-complexed Fe(II);[10] bioreduction with Fe-bearing clays, as well as with biotite and chlorite;[11,12] and Tc(IV) retention in waste forms under high temperatures.[13] One of such approaches is utilization of iron minerals as crystalline media for Tc(IV) incorporation, where an atom of Fe is substituted with Tc. A comprehensive review on Tc immobilization via sorption to various materials is available, where iron minerals are also considered.[14] However, discrepancies in relation to Tc incorporation mechanism into iron minerals structure exist, and have not been discussed previously.

In the environment of rocks and soils, cations of such abundant element as Al can substitute up to one third of Fe(III) in iron oxyhydroxide goethite (α-FeOOH), 0.33 mol/mol, and up to 0.15 mol/mol in iron oxide maghemite (γ-Fe_2O_3) in igneous rocks based soils.[4] Similarities in ionic radii and relatively high electrostatic charge of an ion are the preferential conditions for enrichment of a mineral with different elements.[1] Ionic radius of Fe(III) is known to be, for example, 0.063 nm for 4-coordinate tetrahedral, and 0.0785 nm for 6-coordinate octahedral high spin states, and the ionic radii of substitutional cations are known to range from 0.053 for Al(III) and to 0.092 nm for Cd(II), both 4-coordinate tetrahedral, surpassing the Fe(III) of the same coordination in -16 to +46 % of its size.[4] Hence, Tc(IV) with ionic radius 0.0785 nm, octahedral, identical to Fe(III) octahedral high spin, is expected to have considerable substitutional dissolution in the crystals of iron oxides / oxyhydroxides.

The objectives of this review is two-fold including systematization of the most relevant studies on Tc-incorporated iron oxides/oxyhydroxides (Chapter 2), and clarification of the mechanism of Tc(IV) substitution in magnetite, whether it is Fe(III) sites due to similar atomic radii, or Fe(II) due to natural process of maghematization, oxidation of magnetite (Chapter 3).

2. Comparative analysis of studies on abiotic reductive removal of aqueous Tc with iron oxides/oxyhydroxides

Incorporation of Tc in iron oxides and oxyhydroxides has been demonstrated by a convincing number of studies, which can be described as those with Fe precursors (aqueous Fe(II), iron powder, etc.) for in-situ formation of iron oxidation products in presence of TcO_4^-, and those with certain, already synthesized, iron oxides/oxyhydroxides phases, Table 1. In both types of studies Fe(II), added as aqueous solution or dissolved from iron minerals, serves the role of a strong reductant for Tc(VII) which, being reduced to Tc(IV), directly precipitates as amorphous $TcO_2{\bullet}nH_2O$, characterized by very low solubility of 10E-08,[15] or forms at first soluble polymeric chains of $Tc(IV)nOp^{(4n-2p)+}(H_2O)_q$ with $n > 2$, which precipitate as clusters at $n < 5$ (adsorbed as an isolated complex), or precipitates at $n > 10$ as a separate phase.[16-18] Overall, reduced Tc species follows possible pathway of co-precipitation, surface complexation or surface sorption, and incorporation. Incorporation of Tc(IV) in a crystal structure pertains to more environmentally stable form of sequestered Tc, thus, incorporation of the abiotically reduced mononuclear Tc(IV) into lattice of iron minerals is of the main focus of this review.

Theoretically, reduction of Tc(VII) by aqueous Fe(II), which is referred to as a homogenous reaction (eq 1), is thermodynamically favorable in the near neutral pH, log$K$ = - 13.5 at 298° K,[19,20] however, it was reported to proceed very slowly.[19,21] Tc(VII) was not reduced by aqueous Fe(II) within seven days,[22] but within 26 days the reduction was complete in a system of 11 uM of Tc(VII) and 50 uM $Fe(II)_{(aq)}$;[19] further increase in Fe(II) concentration, up to 800 uM, led to rapid reduction rate accompanied by accumulation of a dark sediment (magnetite and/or maghemite). Transition of homogeneous reduction reaction to heterogeneous occurred at the excess of $Fe(II)_{(aq)}$, when insoluble iron minerals formed allowing Tc(VII) reduction by adsorbed $Fe(II)_{(aq)}$ at the solid-aqueous interface of a mineral.

$$TcO_4^- + 3Fe^{2+} + (n + 7)H_2O = TcO_2 \bullet nH_2O_{(s)} + 3Fe(OH)_{3(s)} + 5H^+ \qquad (1)$$

The reactivity of $Fe(II)_{(aq)}$ is enhanced once it is adsorbed to the mineral surface, possibly through interfacial electron transfer; however it is dependent on compositional and structural characteristics of the iron oxide/oxyhydroxite, i.e. hematite vs goethite, and concentrations of sorbed Fe(II) (sorption density), which are induced at higher pH due to surface complexation by hydroxo ligands, and surface area of minerals.[23] Ferrihydrite possessing a large surface area (> 200 m^2/g;[24] was found to adsorb three times more of aqueous Fe(II) than goethite and hematite,[23] and exhibited stronger reductant properties than such oxyhydroxides as goethite and lepidocrocite.[25] Overall, aqueous Fe(II) adsorbs to crystal growth sites of a substrate mineral, and gets incorporated into its crystal structure,[24,25] yielding, in case of ferrihydrite as a substrate, magnetite or maghemite.[4,19]

Thus, Tc(VII) is instantaneously reduced to Tc(IV) in the reaction with goethite or hematite and aqueous Fe(II), and the reduction products are primarily reported as surface complex or precipitate (octahedral TcO_2 monomers or dimers), associated with crystal nucleation sites of Fe(III) minerals. Isotopically enriched $^{57}Fe(II)_{(aq)}$, added to goethite and hematite and equilibrated for adsorption, was maintained at low concentrations with the purpose to minimize effect of homogeneous reaction of Tc(VII) with aqueous Fe(II).[10] Addition of TcO_4^- into this heterogeneous reaction led to rapid decrease in concentrations of dissolved and total Fe(II) implying on electron transfer Fe(II) – e^- = Fe(III), which exceeded the stochiometric demand for Tc(VII) reduction (Fe(II):Tc(VII) = 3:1, eq. 1) and resulted in electron transfer from Fe(II) to bulk iron oxide/oxyhydroxide on crystal growth sites.[10] Researchers Zachara et al. (2007)[19] also observed decrease in aqueous Fe(II) concentrations in amount that was higher than stochiometric demand for Tc(VII) reduction, and led to formation of poorly crystalline Fe(II)-substituted ferrihydrite, which further transformed to magnetite and/or maghemite. In the control samples containing no Tc, concentrations of aqueous Fe(II) did not change up to 40 days.[19] Reduced Tc species were identified as surface complexes of octahedral dimers on point defects of ferrihydrite.

The effectiveness of induced with aqueous Fe(II) heterogeneous reaction encouraged more studies with $Fe(II)_{(aq)}$ added to goethite, and with Fe(II)-mediated ferrihydrite.[26,27] In these studies $FeCl_2 \bullet H_2O$ supplied Fe(II) in a slurry with goethite,[26] and induced crystallization of ferrihydrite to magnetite.[27] As a result, from 93 to 100% of Tc(VII) was reduced in both DIW and synthetic scrubber solutions (Table 1) and removed predominantly by incorporation of Tc(IV) into lattice of goethite, and, possibly, magnetite that was formed during mineral transformation of newly precipitated $Fe(OH)_{2(S)}$ or during reaction of dissolved Fe(II) with Fe(III).[26] At initial spike of TcO_4^-, Fe:Tc molar ratio in different samples ranged from 452 to 8818 (before addition of 2 M NaOH and Fe(III) armoring); Table 1. All detectable Tc was also removed from the aqueous phase of three types of synthetic cement leachates right after addition of 0.1 M of $Fe(II)_{(aq)}$ to ferrihydrite, followed by incorporation of Tc into newly formed magnetite (0.1 wt.%);[27] initial Fe:Tc molar ratio was around 4700, creating abundance of Fe; Table 1. However, in the study with solid synthesized $Fe(OH)_2$, incorporation of Tc(IV) into newly formed magnetite was estimated about only 17 % (sample without Cr(VI),[28] with $TcO_2 \bullet 2H_2O$ comprising the dominant Tc species. Low incorporation rate might be explained by the relatively low Fe:Tc ratio of 56, and relatively short reaction time in the aerobic environment (Table 1). On the other hand, Kobayashi et al. (2013)[29] reported complete Tc(IV) incorporation in the magnetite structure within two months and at lower pH (6.5-7.0), controlled with 2-(N-morpholino)ethanesulfonate (MES) buffer, Fe:Tc ratio 3090. Reduction of Tc(VII) did not occur in samples with hematite and goethite, given relatively long reaction time; Tc (VII) reduction by Fe(0) powder and Fe(II)/Fe(III) was complete within 3 days, Fe:Tc ratio 120 and 110 respectively, Table 1. However, at pH > 10 pH pertechnetate was not reduced by iron powder; and at pH < 4 it was not reduced in Fe(II)/Fe(III) system. In addition to pH, which controls magnetite's dissolution and recrystallization, resulting in higher Fe(II) concentrations in the pH range 6-7.5 and leading to enhanced incorporation of Tc(IV), variation of TcO_4^- concentration was found to be defining factor for either TcO_2 dimers (polymers) formation or Tc incorporation into crystal structure of iron mineral, given six weeks reaction time.[29,30] TcO_2 dimers bonded to magnetite surface were observed at higher initial concentrations of TcO_4^-, whereas partial Tc(IV) incorporation into magnetite was promoted by lower concentrations of TcO_4^-, Fe:Tc ratios varied from 1300 to 3230;[30] Table 1. Another studies in support of surface complexation was conducted by Pepper et al. (2003),[31] where Tc(VII) was reduced with carbonate and sulfate green rusts, and by Darab et al. (2007),[18] where TcO_4^- was reduced by nano iron and iron powder, Table 1. Iron powder, provided at the excess for one mole of Tc (Fe:Tc = 992), reduced only around 30% of pertechnetate, which might be explained by lower than nano iron surface area and relatively short reaction time (less than two days).[18] Results delivered by Heald et al. (2012)[32] demonstrated corrosion inhibition of iron (i.e., steel) in presence of TcO_4^- and existence of pertechnetate bound to the surface and incorporated into iron corrosion products, even though it was significantly reduced to Tc(IV), Table 1.

It is worth to distinguish a study by Lukens and Saslow (2018),[33] where two Tc-doped iron minerals, magnetite and hematite, were prepared and characterized as immobilizing matrices tested for Tc leaching. Tc was incorporated at 2.5 and 2.2 wt.% into magnetite and hematite respectively, and leaching rates were observed to be $4 \cdot 10^{-5}$ g/(m^2 d) for magnetite and 3 10^{-6}

g/(m^2 d) for hematite. Tc leaching was attributed to the dissolution of iron particles containing incorporated Tc and was limited by solid state diffusion taking place in the iron particles and transporting Tc(IV) to the surface.[33] Diffusion occurs during oxidation of magnetite to maghemite, when Fe(II) diffuses in magnetite particles (maghematization process), and samples doped with Tc reveal higher loss of Fe(II) than samples of magnetite only.

The studies with heterogeneous reaction of adsorbed to mineral surface $Fe(II)_{(aq)}$ reported successful Tc(VII) removal, mainly via co-precipitation, followed by surface complexation or incorporation of Tc and Fe(II) into iron solids. Right conditions for iron mineral transformations, such as dissolution rate/availability of Fe(II), presence of solid phase of Fe(III) or time required for its formation from dissolved Fe(II), pH in case of limited aqueous Fe(II), aerobic environment that oxidizes Fe(II) limiting its availability, would define kinetics and predominance of either process.

Table 1. Selection of the most relevant studies on abiotic TcO_4^- reduction by iron oxides and oxyhydroxides

Source of iron (method of synthesis) and environment	Initial concentration of TcO_4^-, M	Final concentration of TcO_4^-, M	Fe:Tc molar ratio at spike	Reduction time	Background electrolyte	pH	Form of reduced Tc, as defined in the study	Source
Fe(II) aqueous Ar anaerobic chamber	$1.10\cdot10^{-5}$ $1.10\cdot10^{-5}$ $1.10\cdot10^{-5}$	$1.10\cdot10^{-5}$ < LOD < LOD	36.4 36.4 36.4	>1 mo 2 days 1 hr	Na-PIPES buffer	6.0 7.0 8.0	Surface complex of octahedral TcO_2 dimer on ferrihydrite	Zachara et al., 2007
Hematite, goethite and dissolved Fe(II) Ar anaerobic chamber	$1.02\cdot10^{-5}$ $2.05\cdot10^{-5}$	< LOD < LOD	$5.5\cdot10^{3}$ $1.6\cdot10^{3}$	Instantaneous	Na-acetate and PIPES buffer solutions	4.0-7.0	Sorbed to hematite and goethite octahedral TcO_2 monomers and dimers	Peretyazhko et al., 2009
Slurry of synthesized α-FeOOH and dissolved Fe(II) Anoxic chamber	$2.20\cdot10^{-5}$ $4.20\cdot10^{-4}$	$1.61\cdot10^{-6}$[a] $2.60\cdot10^{-5}$[b]	$1.4\cdot10^{4}$[c] $3.8\cdot10^{2}$[d]	1-2 days and 7 days in oven	Deionized water and synthetics scrubber solutions	initial 1.5-1.8 to final 12.9-13.4	Incorporated into goethite and/or magnetite as octahedral Tc(IV)	Um et al., 2011
Fe(II)-induced crystallization of ferrihydrite to magnetite Anaerobic	$3.03\cdot10^{-5}$	< LOD	$4.67\cdot10^{3}$	within minutes	Synthetic leachates: 0.1 M KOH, 0.1 M NaOH, and 1.4 mM $Ca(OH)_2$ 16.2 mM $Ca(OH)_2$ 0.2 mM $Ca(OH)_2$	13.1 12.5 10.5	Incorporated Tc(IV) into magnetite structure	Marshall et al., 2014

$Fe(OH)_{2(S)}$ as a precursor for magnetite Air	$1.01\cdot10^{-5}$[e]	$<5.05\cdot10^{-8}$[f]	56	3 days	1 M NaOH	13.5	Incomplete reduction of Tc(VII); TcO_2 nH_2O precipitate as the dominant phase; partial incorporation ofTc(IV) into magnetite (17 %)	Saslow et al., 2017
Iron powder Magnetite Goethite Hematite Fe(II)/Fe(III) Ar atmosphere	$1.00\cdot10^{-5}$ $2.00\cdot10^{-5}$ $2.00\cdot10^{-5}$ $2.00\cdot10^{-5}$ $1.00\cdot10^{-5}$	< LOD LOD $2.00\cdot10^{-5}$ $2.00\cdot10^{-5}$ $1.00\cdot10^{-7}$	$1.2\cdot10^{2}$ $3.1\cdot10^{3}$ $3.6\cdot10^{3}$ $4.1\cdot10^{3}$ $1.1\cdot10^{2}$	3 days 2 mo 2 mo 1 wk 3 days	0.1 M NaCl	6.0-10.0 6.1-7.5 6.1-7.9 6.0-7.0[g] > 6.0	Negligible sorption of unreduced Tc(VII) to hematite and goethite; incorporation of Tc(IV) into magnetite	Kobayashi et al., 2013
Synthesized magnetite Ar atmosphere	$2.00\cdot10^{-5}$ $2.00\cdot10^{-4}$	< LOD < LOD	$1.4\text{-}3.2\cdot10^{3}$[h] $1.3\text{-}3.2\cdot10^{3}$[i]	6 wks	0.1 M NaCl	8.7-9.3	Partial incorporation of Tc(VII) and formation of sorbed to the magnetite surface Tc(IV) dimers	Yalcintas et al., 2016
Carbonate green rust Sulfate green rust Inert atmosphere	$7.60\cdot10^{-5}$ $7.60\cdot10^{-5}$	$1.52\cdot10^{-7}$[j] $1.52\cdot10^{-7}$	$1.9\cdot10^{3}$[k] $1.8\cdot10^{3}$[l]	Up to 1 day	Deionized water	7-8	Surface complexation of Tc(IV) as TcO_2-like formation	Pepper et al., 2003
Nanoiron Iron powder Air	$9.00\cdot10^{-5}$ $9.00\cdot10^{-5}$	$3.3\cdot10^{-6}$ $6.3\cdot10^{-5}$	$6.6\cdot10^{2}$ $9.9\cdot10^{2}$	1.5 days	Hanford tank waste simulant	n.a.	Surface sorption of isolated TcO_6 octahedra	Darab et al., 2007

Carbon steel coupons Air	$1.00\cdot10^{-6}$ $1.00\cdot10^{-4}$	$<5.00\cdot10^{-7}$[m] not specified	$2.9\cdot10^{7}$ $2.9\cdot10^{5}$	175 days	Simulated $CaCO_3$-saturated groundwater, and tap water	7.4	Incorporation and surface sorption to the corrosion products, both Tc(IV) and TcO_4^-	Heald et al., 2012
Iron powder to produce magnetite and hematite Air	$1.22\cdot10^{-3}$[n] $1.16\cdot10^{-3}$	$2.80\cdot10^{-5}$[o] $2.09\cdot10^{-4}$	49.5 49.5	1 hr 18 hrs	TcO_4^- in 5 M HNO_3 denitrated with HCOOH and contacted with 14.8 M NH_4OH for iron oxide synthesis	final 8.7 3.3	Synthesis of $Tc_{0.06}Fe_{2.94}O_4$ $Tc_{0.03}Fe_{1.97}O_3$	Lukens and Saslow, 2018
Granular zero valent iron Air	$1.70\cdot10^{-2}$	$3.40\cdot10^{-3}$	52.5	20 days	80 mM NaCl	initial 7.0 to final 10.2	Incorporation of Tc(IV) with areas of local enrichment and surface sorption of Tc(IV)	Boglaienko et al., in prep.

a – calculated from the given Tc uptake in goethite 92.7% (sample ‘2-1’);

b – calculated from the given Tc uptake in goethite 93.8% (sample ‘2-3*’);

c – calculated from the given 2.75 g goethite in 250 mL DIW and 0.07 M of $FeCl_2\cdot4H_2O$ and $2.2\cdot10^{-5}$ M Tc (sample ‘2-1’);

d – calculated from the given 2.0 g goethite in 250 mL of synthetic scrubber solution and 0.1 M of $FeCl_2\cdot4H_2O$ and $4.2\cdot10^{-4}$ M Tc (sample ‘2-3*’);

e – calculated given 1 mg/L of Tc;

f – calculated given < 0.5% of initial Tc concentration (sample with Tc only);

g – pH at which redox potential was measured;

h – depending on the solid/liquid ratio of magnetite;

i – the range is based on different solid:liquid ratios of magnetite for given concentrations of Tc;

j – calculated from the given 99.8% of Tc(VII) removal (or 0.2% of Tc left in the solution);

k and **l** – approximate values due to variable molecular weight of green rust; values taken for carbonate green rust 636 g/mol and sulfate green rust 672 g/mol;

m – calculated from given more than 50% reduction of Tc(VII);

n – calculated from given 1.0 mg of Tc-99 and final supernatant 8.3 mL (Tc-doped magnetite) and 8.7 mL (Tc-doped hematite);

o – calculated given 2.3 and 18% percent of Tc left in the final supernatant of Tc-doped magnetite and Tc-doped hematite respectively;

LOD – limit of detection.

3. Investigation of the local environment of Tc in the iron oxide magnetite

As it is discussed in the previous section, upon reduction by iron metal and minerals, Tc(IV) can either sorb on the surface as Tc(IV) oxide mono or dimers,[10,18,19,31] or substitute iron in the lattice of magnetite[27,29] and, possibly, goethite;[26] there exists evidence of both processes occurring simultaneously.[28,30] Differentiation between these mechanisms of Tc association with oxidized iron phase is challenging, due to similar distances between iron atoms in the first and second shell (explained below) of different iron minerals, as well as ambiguity of the structural data analysis, fitting, and interpretation. X-ray absorption spectroscopy, or, more precisely, extended x-ray absorption fine structure (EXAFS), is employed to collect Tc K-edge spectra, followed by Fourier transforms to examine Tc atomic distances to the neighboring atoms with coordination numbers, which comprise the local environment of Tc(IV).

Summary of the EXAFS data analyses from the previously discussed studies is given in Table 2. Presented data aim to discern between incorporation vs sorption in iron oxide magnetite only, as it is the most common iron oxidation product identified in the Tc reduction systems (Table 1). Even though, lattice substitution with Tc was also achieved by direct synthesis of Tc-doped hematite,[33] there are many more studies with magnetite incorporation rather than hematite, providing wider comparison range. Goethite was suggested as another structural host for Tc, as it was the dominant iron mineral formed in the examined samples.[26] However interatomic distances between Tc, Fe and O are similar in goethite and magnetite, and the possibility of predominant incorporation to magnetite was not excluded.[26,30] EXAFS spectra of Tc in both goethite and hematite were analyzed by Peretyazhko et al. (2009)[10] and were found to be almost identical not only to each other, but also to the spectra of ferrihydrite.[19] Overall, it was concluded that EXAFS analysis, presenting average environment of Tc, is unable to discern and precisely determine its structural environment, due to similarities of T(IV)-ferrihydrite, -goethite, and -hematite reference spectra.[10,19]

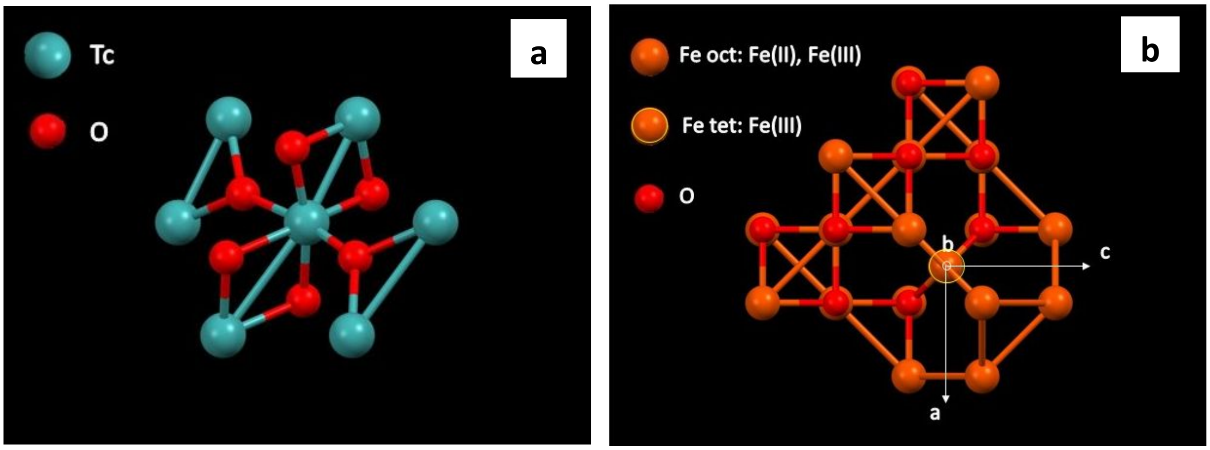

Figure 1. Structure of TcO_2 (a) and Fe_3O_4 magnetite (b); axis 'b' points to the plane of the image. Images created in Mercury 4.0.0 software.

In a reduced form Tc(IV) exists as octahedron, coordinated to 6 atoms of O at distance close to 2.0 Å. This easily discerns it from tetrahedral Tc(VII)O4- with atomic distance to Tc—O at 1.7 Å.[30,33] All reviewed studies agree in resolving spectra with Tc—O distances from 2.0 to 2.03 Å (Table 2) confirming the oxidation state of Tc(IV), which is also supported by XANES measurements.

In magnetite, Tc(IV) octahedron (TcO_6) is linked to 6 octahedral Fe (both Fe(II) and Fe(III) neighbors) with reported Tc—Fe atomic distance within the range 3.02 – 3.13 Å (Table 2) that is referred as the shorter distance in the first shell, Tc—Fe_1, and to 6 tetrahedral Fe(III) at atomic distance reported at 3.46 – 3.54 Å (Table 2) that is the longer distance in the second shell, Tc—Fe_2. Ideally, structural mononuclear Tc(IV) that substitutes octahedral Fe(III) with the identical atomic radii (both are 0.0785 nm), should have Tc—Fe_1 short distance 2.97 Å and Tc—Fe_2 long distance 3.48 Å (corresponding to the structure of magnetite), however it is not observed due to the charge excess and charge compensation mechanism. EXAFS spectra of all reviewed studies yielded Tc—Fe_1 distance being longer than 2.97 Å in magnetite, regardless of Tc(IV) incorporation or sorption mechanism, while Tc—Fe_2 distance did not differ to that extend compared to magnetite (Table 2). Therefore, the atomic Tc—Fe distances in the first and second shell do not provide conclusive evidence of mechanism of Tc association with iron oxide. Moreover, the atomic distance to oxygen in magnetite is around 2.0 Å (Table 2), making it indiscernible for Tc in Tc(IV) oxide, surrounded with six atoms of oxygen at 2.0 Å, from Tc in magnetite (substituting octahedral Fe), surrounded with the same number of oxygen atoms at the same distance.

Data with Tc —Tc at 2.57 Å were explained as signature of existing Tc(IV) oxide mono- and dimers and TcO_2-like clusters ($n < 5$).[10] Coordination numbers (CN) of Tc—Tc were reported at 0.7 for Tc in the goethite and 0.9 for Tc in the hematite samples (both at 2.57 Å). Similarly, for the sorbed Tc dimers identified by Yalcintas et al. (2016),[30] Tc—Tc has CN of 0.9 at 2.57 Å. In the study by Saslow et al. (2017),[28] Tc—Tc with CN of 1.2 at 2.56 Å were reported, and the Tc dominant phase was estimated as about 60% of $TcO_2•2H_2O$ precipitate. Worthwhile to evaluate the study by Lukens and Saslow (2018),[33] where Tc-doped magnetite was synthesized. The fit of EXAFS data also included Tc—Tc (Table 2), despite all Tc was incorporated into the lattice. This study was conducted at relatively high Tc loading (Fe:Tc molar ratio around 50, Table 1), and Tc in magnetite was distributed heterogeneously, with areas of high concentration, which explains Tc—Tc neighbors with high CN (the atomic distance was constrained to equal Tc—Fe_1 of the preceding shell).

Theoretical computational studies were also conducted to investigate incorporation of Tc into iron oxides[35,36] aimed at mechanistic elucidation of Tc structural incorporation and charge compensation. The results suggested that, as Tc(IV) occupies octahedral site in the lattice of magnetite, the most energetically favorable charge compensation mechanism is the removal of two Fe(II) from octahedral sites. This mechanism is similar to the natural process of oxidation of magnetite to maghemite (maghematization), when atoms of Fe(II) leave vacancies on octahedral sites.[35] It was not though supported experimentally, when Fe L-edge X-ray magnetic circular dichroism (XMCD) spectroscopy was employed to investigate Fe(II) and Fe(III) on octahedral and tetrahedral sites in $Tc_{0.1}Fe_{2.9}O_4$.[34] Whereas tetrahedral Fe(III) were equal 1, distribution of octahedral Fe(III) was 0.7 and octahedral Fe(II) was 1.2, suggesting substitution of Fe(III) with Fe(II) to compensate for the charge excess of Tc(IV), which replaces Fe(III) due to similar atomic radii. As mentioned in introduction, it is common that iron atoms can be substituted with different metals surpassing their atomic sizes.[4] Therefore, similarity in atomic radii is not the defining factor, as it is commonly argued.[27-29,34] Moreover, there are several limitations in XMCD analysis, so that at low energy ($L_{2,3}$-edge for Fe) spectra exhibit higher intensity, leading to overestimated Fe(II) content as discussed by Pattrick et al. (2002).[37] This might have occurred in the XMCD measurements by Lukens et al. (2016),[34] which would explain observed mismatch calorimetric analysis in the same study indicating twice lower Fe(II)/Fe(tot) ratio. In addition, important to note that atomic radius of octahedral Fe(II) is 0.092 nm and in case of substitution of Fe(III) by Fe(II) to compensate for the charge of Tc(IV), atoms with larger ionic radii enter the lattice, which leads to its expansion.[34] However, decrease of the lattice is often reported in the Tc-contact samples,[27,28] which is consistent with the process of oxidative maghematization (loss of Fe(II) and creation of vacancies), theoretically supported by Smith et al. (2016).[35] Thus, we argue that, although several pathways for Tc(IV) incorporation into magnetite may exist, the most evident from the theoretical and experimental analyses is substitution of octahedral Fe(II) by Tc(IV) followed by loss of another Fe(II) for the charge balance, which corresponds to the natural process of maghematization of magnetite.

Table 2. Comparison of the EXAFS data analysis for associated with magnetite Tc(IV)

	Magnetite$^{(a)}$		Studies											
			Lukens-2018		Marshall-2014		Kobayashi-2013$^{(b)}$		Um-2011$^{(c)}$		Yalcintas-2016		Saslow-2017$^{(d)}$	
Neighbor atoms	CN	R (Å)	CN^i	R^i (Å)	CN^i	R^i (Å)	CN^i	R^i (Å)	CN^i	R^i (Å)	CN^i/CN^s	R^i/R^s (Å)	CN^m	R^m (Å)
O	**6**	**2.06**	5.3	2.025	6^f	2.00	6^f	2.03	6	2.014	6^f/5.7	2.01/2.02	3.3	2.012
Fe$_1$	**6**	**2.97**	2.7	3.13	4.3	3.04	6^f	3.09	4	3.08	6^f/2.9	3.08/3.12	1.0	3.02
Fe$_2$	**6**	**3.48**	5.3	3.46	4.0	3.48	6^f	3.51	4	3.54	6^f/4.4	3.49/3.52	1.0	3.49
Tc			2.6	3.13^c							/0.9	/2.57	1.2	2.56
O			7.0	3.57	6^f	4.00							1.21	2.44
			Incorporation		Incorporation		Incorporation		Incorporation		Incorporation / sorption		Precipitate and incorporation	

^{i} **- stands for incorporation**, i.e. data interpreted for Tc incorporation mechanism;

^{s} **- stands for sorption**, i.e. data interpreted for Tc sorption mechanism;

^{m} - **stands for mixture**, i.e. data interpreted for Tc sorption and incorporation mechanisms altogether;

$^{f,\ c}$ - parameter fixed or constrained;

(a) – Lukens et al. (2016); Marshall et al. (2014);

(b) – sample with pH 7.5;

(c) – sample '2-3*';

(d) – sample with Tc only;

CN – coordination number;

R – atomic distance (R+ΔR).

4. Summary

The comparative review of the selected range of studies describing abiotic Tc(VII) reduction with iron oxides and oxyhydroxides, such as magnetite, hematite, goethite, and ferrihydrite, revealed co-existence of several processes upon reduction of pertechnetate anion (Tc(VII)O_4^-) that can be detected simultaneously: polymerization of Tc(IV) into chains of Tc(IV) oxide that might create clusters and precipitate on the surface of iron mineral as TcO_2 mono or dimer complexes; surface sorption of Tc—Tc dimers; and incorporation of Tc(IV) into lattice structure of iron oxides, i.e. predominantly magnetite. The mechanism for mononuclear incorporation of Tc(IV) into magnetite is discussed, and it is demonstrated that Tc(IV) substitution of Fe(II) with consequent loss of Fe(II) for the charge mismatch is more evident, despite commonly accepted assumption of Tc(IV) for Fe(III) substitution due to similarity in atomic radii. Oxidation of Fe(II) and creation of cavity during Fe(II) loss is described by the natural process of maghematization (transfer of magnetite to its fully oxidized state, maghemite), and Tc(IV) incorporation during this process is more energetically favorable, as it was supported before through computational studies. Clarification of the Tc local environment in iron minerals via EXAFS data analysis does not produce a definitive answer, as the local environment in different iron oxides and hydroxides is very similar and may not be taken alone for the conclusive statements. It is recommended not to rely on the EXAFS analysis only, but to complement it with other techniques.

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This article reviews the mechanism of Tc incorporation into crystal structure of magnetite and provides comparative EXAFS analysis.