



Interaction of niobium with iron-oxide colloids and the role of humic acid



Madhusudan Ghosh ^{a, b, *}, K.K. Swain ^{a, b}, Rakesh Verma ^c

^a Homi Bhabha National Institute, Anushaktinagar, Mumbai, 400094, India

^b Analytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai, 400085, India

^c Formerly Analytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai, 400085, India

ARTICLE INFO

Article history:

Received 24 May 2017

Received in revised form

7 August 2017

Accepted 8 August 2017

Keywords:

Iron-oxide

Niobium

Humic acid

Sorption

Radioactive waste

ABSTRACT

In this work, we report the sorption of Nb on iron oxides and the effect of humic acid. Iron oxides viz. goethite, hematite and magnetite were chemically synthesised and characterised by X-ray diffraction, particle size, surface area and zeta potential measurement. The sorption of Nb on all the three iron oxides was low (~40%) at pH 1, increased to ~90% at pH 8 and decreased marginally above pH 8. The effect of humic acid on the sorption was very small. Thermodynamic parameters viz. activation energy, enthalpy, entropy, free energy and sticking probability were calculated to understand the mechanism of the sorption process. Although the enthalpy was positive, the free energy change was negative i.e. the sorption was entropy driven process. The sorption followed pseudo-second-order kinetics and sticking probability model indicated that the process was chemisorption. This study is important to understand the probable migration of ⁹⁴Nb (half life 20300 y) during underground storage of radioactive waste.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Zr-2.5 wt% Nb alloy is used as pressure tube material in Indian pressurized heavy water reactors because of its excellent mechanical strength [Howe-Grant, 1996] and very high resistance to hydride attack [Lister, 1992]. ⁹⁴Nb (half life 20300 y) is formed by ⁹³Nb(n,γ) ⁹⁴Nb reaction in pressure tubes and the steel components of the fuel assemblies. ^{93m}Nb (half-life 16 y) is another radioisotope of Nb in the spent nuclear fuel continuously formed by decay of ⁹³Zr (half-life 1.5 × 10⁶ y) and ⁹³Mo (half-life 4000 y). Calculation shows that after a residence time of 10 y inside a nuclear reactor having a neutron flux of 10¹⁴ cm⁻² s⁻¹, discharged pressure tubes will contain about 10¹⁰ Bq of ⁹⁴Nb per kilogram of Zr-Nb alloy. Along with the above said radionuclides, the presence of fission products and other activation products in discharged pressure tubes results in a large radiation field. After 8–10 years of cooling period, the short-lived and most of the medium-lived radioisotopes (half-life: ≤ 1.5 years) decay off [Gangotra et al., 2002].

Pressure tubes are removed from a nuclear reactor after 10 effective full-power years or subsequent to their failure. The

discharged pressure tubes from Indian power reactors are currently kept in deep tile holes having concrete caps. The release of radionuclides from the final disposal to the groundwater and their subsequent migration from the geosphere to the biosphere is of great importance in the safety assessment of radioactive waste disposal method [OECD, 1984]. The groundwater velocity and distribution of radionuclides between stationary phase (aquifer solid) and groundwater are the two main parameters controlling the migration rate. The migration of elements with very low aqueous solubility and strong sorption on aquifer solid has been explained by colloidal-facilitated transport model [Nelson and Orlandini, 1986; Kersting et al., 1999]. The model consists of three phases namely stationary aquifer solid; the mobile aqueous phase and non aqueous mobile colloids. Both inorganic and organic materials such as mineral and weathering products, humic substances, and microorganisms are known to exist as colloids in ground water. The chemical composition, size distribution and formation kinetics of aquatic colloids and their aggregates has been discussed by Buffle and Leppard (1995). McCarthy and Zachara have discussed the role of colloids in transport of contaminants [McCarthy and Zachara, 1989].

* Corresponding author. Analytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai, 400085, India.

E-mail address: ghoshm@barc.gov.in (M. Ghosh).

Table 1
Thermodynamic parameters of Nb sorption on iron oxides.

Thermodynamic parameters	Goethite	Hematite	Magnetite
ΔG^0 (kJ M ⁻¹)	-3.4	-1.7	-4.2
ΔH^0 (kJ M ⁻¹)	9.7	13.9	14.5
ΔS^0 (J K ⁻¹ M ⁻¹)	48	57	69
Activation energy (kJ M ⁻¹)			
Acid medium (pH = 1)	11.6	15.6	19.8
Basic Medium (pH = 10)	10.5	14.3	18.4
Sticking probability (S [*])	0.002	0.001	0.0002

Niobium (Nb) is one of the high priority elements when considering its possible migration into the biosphere because of its low solubility in neutral and slightly alkaline regions [Haapanen et al., 2009; Hjerpe et al., 2010]. Nb belongs to the VA group of elements in the periodic table and +V is the most stable among its four oxidation states ranging from +II to + V. Nb occurs in soils and ground waters in +V state even in highly reducing conditions [Baes and Mesmer, 1976; Lehto and Hou, 2010; Steinberg, 1961]. Nb forms complex ions in solutions owing to its high ionic potential. In acidic solution, the principal chemical form is NbO₂⁺, while neutral species (HNbO₃ or Nb(OH)₅) occur in slightly acidic to neutral solutions. Anionic species (NbO₃⁻ or Nb(OH)₆⁻) are predominated above pH 7 [Lehto and Hou, 2010; Andersson et al., 1979]. The very low solubility of Nb is due to its tendency to hydrolyse. Niobium has strong tendency to form complex with fluoride, citrate and oxalate anions [Steinberg, 1961; Charles and Prime, 1983]. Sorption of Nb on colloids and its tendency to form intrinsic colloids has been found to be significant [Lehto and Hou, 2010; Steinberg, 1961]. Association of Nb with colloidal iron and dissolved humic substances in natural waters has been observed [Åström et al., 2008]. Niobium can also form negatively charged colloids in aqueous solutions with the chemical properties of Nb₂O₅ oxide. In 0.5 M HNO₃ medium there is no intrinsic colloid formation of Nb at a concentration of 10 × 10⁻⁸ M, whereas colloids were formed at 7–9 × 10⁻⁶ M and increased with increase in Nb concentration [Lin et al., 1990]. Significant sorption of Nb on colloids generated from clay material has been reported [Baston et al., 1992].

The common colloids present in the ground water are hydrous oxides of silica, alumina and iron whereas most important natural ligands are humic acids (HA). The presence of HA may affect the sorption and migration of radionuclides in the ground water. It is reported that the anthropogenic actinides are about 10 times more concentrated in HA fraction than in the overall top soil [Buckau, 2005]. The interaction of HA with radionuclides increases the mean residence time of the actinides in the mobile phase and reduce the sorption of radionuclides to stationary phase (aquifer solid) causing enhanced migration [Buckau, 2005]. Also, HA can alter the oxidation state of the metal e.g. in the presence of HA U(VI) and Np(V) are reduced to U(IV) and Np(IV) respectively [Buckau, 2005].

The lack of knowledge concerning interaction of Nb with different soil components provided us with the motivation to carry out systematic study on its sorption behaviour with natural colloids using batch method. The aim of the present work was to study the sorption of Nb on iron oxides and effect of HA on the sorption. Sorption behaviour in neutral to slightly alkaline conditions was of special interest to understand the sorption process in this region where the neutral species turns into the anionic one. Kinetics of sorption was investigated and thermodynamic quantities viz. activation energy, enthalpy and free energy were determined to elucidate the mechanism of sorption.

2. Material and methods

2.1. Materials

XAD-4 (20–60 mesh), sodium perchlorate (NaClO₄) and sodium salt of HA from Sigma Aldrich, ferric chloride, FeCl₃ (LR, Laba chemie), sodium hydroxide, NaOH (Thomas baker), ammonium hydroxide, NH₄OH (S D Fine Chem), ferrous ammonium sulphate, (NH₄)₂SO₄.FeSO₄.6H₂O (Sarabhai Chemicals), glacial acetic acid, CH₃COOH (Chemco fine chemicals), acetone (Extra pure AR, Sisco Research laboratory) and perchloric acid, HClO₄ (Otto chemie Pvt. Ltd.) were used for this study.

2.2. Synthesis of goethite, hematite and magnetite

Magnetite was synthesized [Schwertmann and Cornel, 2000] by dissolving equal amounts of (NH₄)₂SO₄.FeSO₄.6H₂O and FeCl₃ separately in glass beakers. Solutions were mixed, ammonia solution was added, and stirred continuously at 80 °C for 2 h. The precipitate was filtered, washed with dilute NH₄OH followed by water and finally with acetone. The washed precipitate was heated in oven at 100 °C for 12 h to convert the hydroxides to oxide.

For synthesis of goethite [Schwertmann and Cornel, 2000], about 40 g of FeCl₃ was dissolved in water. Sodium hydroxide solution was added slowly to the FeCl₃ solution followed by heating at 70 °C with stirring for 2 h. A thick yellowish precipitate appeared which was filtered and washed with glacial acetic acid and followed by water. The precipitate was air dried and grinded in acetone.

For synthesis of hematite [Schwertmann and Cornel, 2000], the procedure was similar to that of goethite except the heating. Precipitate thus formed was washed with water until the pH of washings was neutral. Precipitate was heated at 300 °C in a quartz disc for 36 h, cooled and grinded in acetone.

2.3. Characterisation of iron oxides

2.3.1. X-ray diffraction (XRD) measurements

The powder XRD pattern of iron oxides were recorded on a Philips X-ray diffractometer (PW1710 model) with Ni filtered Cu-K_α radiation.

2.3.2. Surface area measurement

The specific surface area was measured by an indigenous surface area analyzer (BARC make) using single point BET (Brunauer–Emmett–Teller) method [Fagerlund, 1973]. About 25 mg of accurately weighed iron oxide was heated electrically at about 110 °C in a glass sample cell for nearly 4 h in continuously flowing mixture of nitrogen and helium. The sample was then cooled to liquid nitrogen temperature in a continuously flowing mixture of nitrogen and helium. The adsorbed nitrogen was desorbed by bringing the sample to room temperature. The changes in the nitrogen concentration of the flowing gas stream, consequent to the adsorption and desorption, were monitored by a thermal conductivity bridge. The desorption signal was electronically integrated from which the surface area of the sample was computed.

2.3.3. Particle size measurement

Colloidal iron oxides were ultrasonicated (Retsch GmbH, Germany) (1 min, 35 kHz, power = 140 W) and transferred to a quartz cuvette (universal 'dip' cell). It was assumed that the soft conditions of ultrasonication would not have altered particle size. Dynamic light scattering (DLS) technique was used for measurement of particle size. The measurements were made at an angle of 130° using Malvern 4800 Autosizer employing a 7132 digital correlator and the light source was He-Ne laser operated at 632.8 nm with

Download English Version:

<https://daneshyari.com/en/article/5477425>

Download Persian Version:

<https://daneshyari.com/article/5477425>

[Daneshyari.com](https://daneshyari.com)