



Engineered materials as potential geocatalysts in deep geological nuclear waste repositories: A case study of the stainless steel catalytic effect on nitrate reduction by hydrogen



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ABSTRACT

The reduction of NO_3^- in natural waters is commonly promoted by biological activity. In the context of deep geological nuclear waste repositories with potentially high H_2 pressure, abiotic redox reactions may be envisaged. Here, the catalytic effect of “inert” metallic surfaces, in part used for nuclear waste canisters, on NO_3^- reduction under H_2 pressure is evaluated. The study is focused on stainless steels by testing the 316L and Hastelloy C276 steels. A parametric kinetic study ($0 < P(\text{H}_2) < 10$ bar, $0.1 < [\text{NO}_3^-] < 10$ mM, $90 < T^\circ < 150$ °C, $4 < \text{pH}_{in situ} < 9$) reveals that NO_3^- reduction, in the presence of stainless steel 316L and Hastelloy C276, proceeds via a pH-independent reaction requiring H_2 as an electron donor. No corrosion of these steels is observed indicating a true catalytic process. The reaction is inhibited in the presence of PO_4^{3-} . Activation energies assuming a first-order reaction in the 90–150 °C temperature range are found to be 46 kJ/mol for stainless steel 316L and 186 kJ/mol for Hastelloy C276, making the reaction efficient at lower temperature and on a human time scale.

Nitrate sorption at the metallic surface being thought to be the limiting step, sorption and competitive sorption isotherms of several oxyanions were performed at 90 °C on 316L. Nitrate and PO_4^{3-} are more strongly sorbed than SO_4^{2-} , likely as inner sphere complexes, and in a large pH range, from acidic to pH 9. The Langmuir–Hinshelwood formalism best fits the kinetic data. The nature of the surface complex, and the competition for sorption between NO_3^- and PO_4^{3-} account for the macroscopic features of NO_3^- reduction by H_2 observed at the steel surface. It should be stressed that some engineered materials such as stainless steels should be considered both as geological material and as geocatalysts as they could remain in the environment over an extremely long period of time.

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1. Introduction

The abiotic NO_3^- reduction reactions are well documented in the context of groundwater de-contamination (Murphy, 1991; Huang et al., 1998; Fanning, 2000; Prüsse and Vorlop, 2001) and early Earth prebiotic syntheses, such as the Strecker synthesis (Summer, 2005; Smirnov et al., 2008; Singireddy et al., 2012). It is also a major reaction of interest in the nuclear repository context (Cox et al., 1994; Honda et al., 2006; Albrecht, 2008; Katsounaros et al., 2009; Truche et al., 2013) where some types of intermediate level, long-lived wastes, are characterized, amongst others by the coexistence of oxyanions (NO_3^- , PO_4^{3-} , SO_4^{2-}) and potential reducing agents such as organic matter, native metals, steels and H_2 gas. In a deep geological waste repository, H_2 is mainly produced by anoxic corrosion of the metallic components (the primary waste containers made of

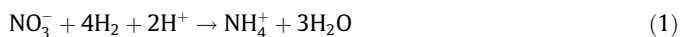
regular cast iron as well as armored cement over packs), and its pressure can reach a maximum theoretical value of 90 bar (Talandier et al., 2006; Xu et al., 2008). Nitrates are found in large concentrations in a variety of waste classes and waste matrices (i.e. bitumen, concrete, compacted salt) as a consequence of spent nuclear fuel reprocessing. The evolution of NO_3^- concentration in space and time in such an environment must be taken into account in the safety assessment because of the multiple possible impacts. It is well known that the NO_3^- has high chemical stability, in order to react with a suitable reducing agent to form N_2 or NH_3 , special conditions such as surface catalysis, microbial activity or high temperature are required (Fanning, 2000). In a deep geological repository, temperatures are not expected to raise above 90 °C, but dedicated assessment is required to consider the consequence of: (i) enzymatic reactions controlled by microbial activity (Van Loosdrecht and Jetten, 1998; Albrecht et al., in press), leading to the formation of N_2 (Van Loosdrecht and Jetten, 1998), or (ii) specific surface catalysis essentially leading to the formation of NH_4^+

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(Fanning, 2000). The multiplication of electron donors, and N-reduced species make it necessary to limit any specific experimental study to a well-defined subject of interest.

In this manuscript the focus is on the abiotic catalytic mechanism in which a plausible reaction with H₂ would result in the increase of pH as well as NH₄⁺ production (Eq. (1)). Ammonium is of additional interest because it can affect the adsorption capacity of clay minerals (Missana et al., 2004) present in natural and engineered barriers for radioactive waste confinement, and thus the mobility of some radionuclides such as ¹³⁵Cs. Ammonium formation can also enhance concrete degradation and reduce its durability (Carde et al., 1997).



Surprisingly, the direct reduction of NO₃⁻ by H₂ is weakly documented. Cox et al. (1994) investigated thermochemical NO₃⁻ reduction by H₂ under strong hydrothermal conditions (360 °C) and pH 4. Under these conditions, 18% of the NO₃⁻ conversion into N₂ was measured in 2 h elapsed time, but the probable thermal degradation of NO₃⁻ and the reactivity of the steel reactor incite caution. However, numerous experimental observations demonstrate that H₂ can have a significant role in the NO₃⁻ reaction mechanism and chemical kinetics at much lower temperature, when metallic phases are present. For example, Siantar et al. (1996) reported that Fe powder pre-exposed to a 10% H₂ atmosphere reduced NO₃⁻ faster than without pre-treatment, suggesting that H₂ penetrated the metal during the pre-exposition and was more readily available in the subsequent experimental run. Huang et al. (1998) also considered that H₂ produced by Fe(0) corrosion, and sorbed at its surface, constitutes a better electron donor than Fe(0) itself.

Some of the most interesting observations concerning the combined role of H₂ and different metals or alloys in NO₃⁻ reduction have been made either using Ni and Fe metals and their alloys (Smirnov et al., 2008) or Pd–Cu bimetallic catalysts (Vorlop and Tacke, 1989; Hörold et al., 1993; Pintar et al., 1996, 1998; Prüsse and Vorlop, 2001; Pintar and Batista, 2007). Pintar et al. (1996) have shown that NO₃⁻ is reduced to NH₃ within minutes even at 20 °C, in the presence of both H₂ and a Pd–Cu bimetallic catalyst. They proposed an intrinsic rate expression for NO₃⁻ reduction based on the conventional Langmuir–Hinshelwood kinetic approach, considering both equilibrium NO₃⁻ as well as dissociative H₂ adsorption processes occurring at different types of active surface sites. They also assumed an irreversible bimolecular surface reaction between adsorbed reactant species to be the rate-controlling step. The apparent activation energy for catalytic liquid phase NO₃⁻ reduction in the temperature range 7.5–20 °C, was found to be 47 kJ/mol. Prüsse and Vorlop (2001) developed a mechanistic model to describe the catalytic activity of bimetallic Pd catalysts toward NO₃⁻ reduction. The NO₃⁻ reduction activity is determined by bimetallic ensembles, at which NO₃⁻ is adsorbed and reduced to NO₂⁻ by H₂ supposed to spillover from the Pd site to the neighboring bimetallic site. Nitrite is further re-adsorbed at the Pd ensembles, where it is reduced to NH₃ or N₂. Smirnov et al. (2008) observed that NH₃ production increases by unit of time in the presence of H₂ at 200 °C. They speculated that in the presence of Ni(0), Fe(0), Ni_xFe_x metal-alloys, a surface mediated reduction reaction may proceed via co-sorption of NO₃⁻ and H₂: H₂ being added artificially in the system or produced *in situ* as a result of interactions between a pristine metallic surface and H₂O. In this scenario, metals and metal-alloys act both as reactants and catalysts. The reaction is facilitated by the activation of one or all of the reactants sorbed onto the surface, thus lowering the energy barrier.

It is concluded that in the case of nuclear waste storage, engineered materials such as stainless steel present in the waste canister

architecture must be considered both as potential catalysts and as geological materials remaining for hundreds of thousands years in the environment. In this environment as modified by human action, the reactivity of these materials on a geological time scale must be evaluated both in the light of chemical engineering and geochemistry. Relatively little research has been conducted to determine the catalytic effect of common minerals or engineered materials on geological and/or environmentally relevant reactions despite the fact that many important reactions may depend on the availability of suitable geocatalysts. Catalysis science, even if relevant for redox reactions, is poorly exploited in the Earth Sciences, in particular at the interface of natural and engineered systems.

In this contribution the catalytic potential of stainless steel surfaces of waste canisters on NO₃⁻ reduction under H₂ pressure is evaluated. A parametric study is reported covering the nature of the steel (Stainless Steel 316L, Hastelloy C276), the H₂ pressure (0–7.5 bar), the NO₃⁻ aqueous concentration (0.1–10 mM), the temperature (90–150 °C) and pH (4–9). The given ranges are based on estimations made for nuclear waste storage safety assessment. Only the temperature range does not reflect values likely for an intermediate level waste cell, where temperatures are not expected to increase above 90 °C. Higher temperatures enhance reaction kinetics and reduce reaction times; they have been chosen to study the reaction kinetics within a specified timeframe.

The objectives of this experimental study are to unravel some of the reaction complexities of abiotic NO₃⁻ reduction, in particular: (i) to evaluate the combined role of H₂ and different types of inert stainless steels likely to be present in geological nuclear waste repositories (Stainless Steel 316L and Hastelloy C276), (ii) to quantify the reaction kinetics following a parametric approach (temperature, pH, H₂ partial pressure, surface site concentration, initial NO₃⁻ concentration, and influence of additional oxyanions such as SO₄²⁻, CO₃²⁻ and PO₄³⁻), and (iii) to investigate reaction mechanisms in the light of sorption studies, inhibitor discovery and comparison between the different types of steels.

2. Experimental method

Batch experiments of NO₃⁻ reduction by H₂ in the presence of stainless steels were carried out in hydrothermal reactors in the 90–150 °C temperature range (±1 °C). The experimented systems involved three phases: (1) an aqueous NO₃⁻-bearing solution (KNO₃ at 0.1–10 mM), (2) powder or chips of Stainless Steel 316L (316L) or Hastelloy C276 (see Table 1 for chemical compositions) and (3) an Ar–H₂ gas phase assuring 0–7.5 bar H₂ partial pressure. The progress of reaction was monitored by successive sampling of the solution during the course of the experiments. In a few experiments, smectite or gaseous CO₂ was added as pH buffers, and other potential inhibiting or poisonous species (SO₄²⁻, S²⁻, CO₃²⁻, PO₄³⁻ or silicic acid) were added to the solution.

A complementary set of experiments was dedicated to the evaluation of the competitive sorption of SO₄²⁻, PO₄³⁻ and NO₃⁻ onto the steel surface. The main lines of the protocol are presented below and additional experimental details are given in the [Supplementary data](#).

2.1. Nitrate/steel/H₂ kinetic experiments

The 316L steel was reacted in an inert 450 mL Parr[®] stirred reactor made of pure Ti grade 4 (Ti-reactor). The specific surface areas of the steel samples were 2.6(±0.2) × 10⁻² m²/g for powders (BET measurements on a Coulter SA 3100 apparatus – solids outgassed overnight at 100 °C down to 2 μm Hg pressure before analysis with Kr as sorbent gas) and 1.1(±0.2) × 10⁻³ m²/g for metal chips (geometric consideration), with no significant variation dur-

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