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On the catalytic effect of Pd(s) on the reduction of UO_2^{2+} with H_2 in aqueous solution

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Abstract

The catalytic effect of Pd(s) (as a model for noble metal particles) on the reduction of UO_2^{2+} by H_2 has been studied experimentally. The experiments were performed in aqueous solution in an autoclave. The aqueous solutions were pressurized with H_2 or N_2 and the UO_2^{2+} concentration was measured as a function of time. The experiments clearly show that Pd catalyzes the reaction between UO_2^{2+} and H_2. The rate constant of the reaction was found to be close to diffusion controlled and independent of the H_2 pressure in the range 1.5–40 bar. The effect of a catalyzed reduction of U(VI) to U(IV) in the solid phase is also discussed.

1. Introduction

In Sweden, the radioactive spent nuclear fuel will be placed in a deep repository according to the KBS-3 model, developed by The Swedish Nuclear Fuel and Waste Management Co, SKB. The fuel will be encapsulated in canisters made of copper with an insert of steel, surrounded by bentonite clay and placed 500 m under the ground. One of the key questions for the safety assessment of the spent nuclear fuel repository is the rate of radiation induced dissolution of the fuel matrix, UO_2, followed by the subsequent release of actinides and fission products. In the event of canister failure, the highly radioactive spent nuclear fuel will cause radiolysis of the groundwater. Radiolysis of groundwater will produce both oxidants ($OH^{\cdot}$, H_2O_2, $HO_2^{\cdot}$ and O_2) and reductants (e_{aq}^-, $H^{\cdot}$ and H_2). For kinetic reasons, the oxidants will react with UO_2 producing soluble U(VI). The most important oxidant under deep repository conditions has been shown to be H_2O_2 [1]. As H_2O_2 is both radiolytically produced and consumed by reduction at the fuel surface, the concentration of H_2O_2 will eventually approach a steady state. The time to approach the surface steady state concentration is sufficiently short to be neglected compared to the times of interest when considering a deep repository [2].

HCO_3^- present in the groundwater increases the otherwise slow dissolution of the fuel matrix due to formation of water soluble complexes with UO_2^{2+} formed upon oxidation of UO_2 [3]. Swedish groundwater contains ~2 mM carbonate [4]. The effect of HCO_3^- on H_2O_2 induced oxidative dissolution of UO_2 is a linear increase of the rate as a function of $[HCO_3^-]$ from 0 to 1 mM. Above 1 mM the rate is independent of the HCO_3^- concentration and the reaction is limited by oxidation [5]. Under these conditions, the surface area available for oxidation can be considered constant with time.

Due to anaerobic corrosion of the iron in the canister large amounts of H_2 are expected to be produced in case of canister failure [6]. H_2 is also produced in the radiolysis of water. Experiments on spent fuel, MOX and α-doped UO_2 show that the dissolution rate is lower than expected from the amount of H_2O_2 produced radiolytically. These experiments were performed at various hydrogen pressures and indicate that the oxidative dissolution rate is reduced in the presence of dissolved hydrogen, but the mechanism is still largely unknown [7]. H_2 slowly reduces U(VI) to

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U(IV) and it also reacts with the radiolytically produced oxidants [8]. However, these effects are of marginal importance and cannot explain the dramatic reduction in dissolution rate.

Some of the fission products in the spent fuel form nanometer sized noble metal particles, often referred to as ε-phase or ε-particles, containing Mo, Ru, Tc, Pd and Rh [9]. The content of noble metal particles in spent nuclear fuel is estimated to be ~1% [10]. From previous experiments these particles are known to catalyze reductions by H_2 [11]. In a recent study we showed that Pd catalyzes the reduction of H_2O_2 by H_2. Even though the catalysis is very efficient, this reaction would only have a small effect on the dissolution rate. One percent surface coverage of Pd would reduce the rate by a factor 3.9 [12].

It is also possible that Pd catalyzes the otherwise slow reduction of U(VI) to U(IV) by H_2. This will not affect the dissolution rate, but it will lower the concentrations of redox sensitive radionuclides in the aqueous phase. The reduction of UO_2^{2+} by H_2 has been studied before and the activation energy for the reaction has been found to be 130 kJ/mol [8]. The reaction was also studied in the 1950s using nickel as a catalyst resulting in an activation energy of 41 kJ/mol [13]. Cobalt and platinum were also shown to catalyze the reaction. Even UO_2 has been suggested to catalyze the reaction, but recent experiments have not supported this theory [8].

In this work we have studied the possible catalytic effect of Pd (as a model for noble metal particles) on the reduction of UO_2^{2+} by H_2 at room temperature.

2. Experimental

All experiments were performed in a glass vessel placed inside an autoclave. The autoclave is equipped with inlet and outlet tubes for pressurizing and sampling and also a stirrer. The Pd powder and 280 ml 2 mM $NaHCO_3$ was bubbled with N_2 for 20 min. The mixture was put in the autoclave and N_2 was blown through for 10 min. The autoclave was then pressurized with H_2 and left overnight with continuous stirring. The amount of Pd powder was varied between 0 and 35 mg. The following day, 20 ml 1.5×10^{-4} M $UO_2(NO_3)_2 \cdot 6H_2O$ solution was added to give a final concentration of 1×10^{-5} M. The concentration of UO_2^{2+} was measured as a function of reaction time for at least 90 min using UV/visible spectroscopy. The concentration was measured with the reagent Arsenazo III (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo-2)-phenylarsonic acid]). Arsenazo III forms colored 1:1 complex with a number of 2+ and 3+ charged cations, for example UO_2^{2+}. The UO_2^{2+}-Arsenazo III complex absorbs at 653 nm. The sample volume taken for analysis was approximately 3 ml to enable doublet samples. Detailed information about the Arsenazo III method can be found in Refs. [14,15].

In order to study if the possible catalytic effect was dependent on the H_2 pressure, experiments were performed with 33 mg Pd varying the H_2 pressure between 1.5 and 40 bar. Experiments without H_2 were also performed. Chemicals and gases came from Merck, AGA and Air Liquid. Milli-Q filtered water was used throughout and all experiments were performed at room temperature.

3. Results and discussion

In the experiments with UO_2^{2+}, Pd and H_2, the concentration of UO_2^{2+} was decreasing with reaction time indicating a catalytic effect of Pd. This is illustrated in Fig. 1. The concentration of UO_2^{2+} did not change with time in the absence of Pd or H_2. The rate of the reaction is increasing with the amount of Pd.

By plotting $\ln([A]/[A]_o)$ against the reaction time we obtain the pseudo-first-order rate constants, k_1 (s^{-1}) from the slopes. The resulting pseudo-first-order rate constants are given in Table 1. By plotting k_1 (s^{-1}) against the solid surface/total solution volume, S/V (m^{-1}) the second order rate constant, k ($m\,s^{-1}$), is determined from the slope. This is shown in Fig. 2. The second order rate constant is $(1.5 \pm 0.1) \times 10^{-5}\ m\,s^{-1}$, which corresponds to the diffusion limit of the system and an activation energy close to zero. The activation energy does not differ significantly from the Pd catalyzed reaction between H_2O_2 and H_2, for which the rate constant was found to be $(2.1 \pm 0.1) \times 10^{-5}\ m\,s^{-1}$ [12]. The solid surface area was calculated using the average particle radius (0.625 μm) assuming spherical geometry.

When varying the H_2 pressure between 1.5 and 40 bar at room temperature we could not observe any increase in the

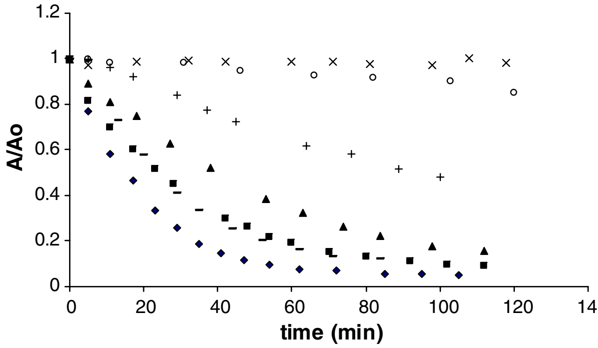

Fig. 1. Normalized concentration of UO_2^{2+} plotted against reaction time at 40 bar H_2 with different amounts of Pd (+ 4 mg, ▲ 8 mg, ■ 16 mg, – 24 mg, ◆ 35 mg, × 32 mg Pd without H_2 (N_2 instead), ○ without Pd).

Table 1
Pseudo-first-order rate constants for different amounts of Pd (S/V ratios) at 40 bar H_2

Pd (mg)	S/V (m^{-1})	k_1 (s^{-1})
4	5.33	1.35×10^{-4}
8	10.67	2.79×10^{-4}
16	21.33	4.52×10^{-4}
24	32	5.88×10^{-4}
35	44	7.83×10^{-4}

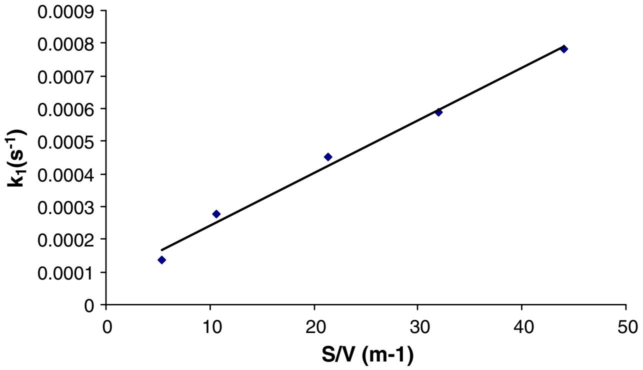

Fig. 2. Pseudo-first-order rate constants, k_1 (s^{-1}), plotted against the solid surface area/total solution volume ratio, S/V (m^{-1}) at 40 bar H_2.

reaction rate. In the previous experiments where nickel was used as a catalyst, the rate of the reaction was found to be directly proportional to the hydrogen pressure [13]. An explanation to why this effect is not seen here could be that Pd can absorb significant amounts of H_2, up to 935 times its own volume [16]. Hence, the dynamics of H_2 absorption does not affect the reaction rate under the present conditions.

As shown above, Pd catalyzes the reduction of U(VI) to U(IV) by H_2 in solution. For 100 year old fuel and 38 MWd/kg burnup, the maximum dissolution rate is expected to be 4.94×10^{-10} mol m^{-2} s^{-1} based on a steady state approach for H_2O_2 [17]. Under these conditions, the U(VI) steady state concentration in solution (i.e. the concentration at which the rate of dissolution of U(VI) is equal to the rate of U(VI) reduction by H_2) is ~3 μM, assuming a noble metal particle content of 1% and 40 bar H_2.

The catalytic effect of noble metal particles studied here is not expected to affect the dissolution of the spent nuclear fuel. But if the same reaction occurs in the solid phase, this would inhibit the dissolution of the fuel much more efficiently. In the solid phase, noble metal particles can catalyze the reduction of undissolved oxidized UO_2 by H_2, thus preventing dissolution of the oxidized UO_2. This requires galvanic coupling between the UO_2 matrix and the noble metal particles. This coupling has been verified in electrochemical studies on SIMFUEL [18]. The noble metal particle catalyzed reduction (which is most likely diffusion controlled [12]) will compete with dissolution of oxidized UO_2. The rate of the latter reaction depends on the HCO_3^- concentration. This would explain why the dissolution in the presence of H_2 is slower than expected. By putting the reduction rate of U(VI) in the solid phase equal to the oxidation rate of U(IV), one can calculate that a noble metal particle content of only 1 ppm on the surface is enough to completely cancel the dissolution (40 bar H_2, 100 year old fuel). Previous long term leaching experiments on spent nuclear fuel indicate that the rate of dissolution approaches zero at 0.1 bar H_2 (produced from radiolysis) [19]. Experiments are now being performed using solid Pd-doped UO_2 pellets to quantitatively examine the inhibiting effect of H_2 on oxidative dissolution proposed above.

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