



Development of a new method for investigating the mechanisms of solid particle dissolution in nitric acid media: Millifluidic study using fluorescent indicators

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ABSTRACT

A key step in existing industrial recycling processes for spent nuclear fuel, after cutting up the spent fuel assemblies, is the continuous dissolution of uranium dioxide in a dissolver containing concentrated nitric acid. The purpose of this study is to enhance our understanding of the phenomena governing the oxide behavior during dissolution, and to acquire new experimental data suitable for modeling and optimizing spent fuel dissolution. The approach adopted involved small scale experiments, which are indispensable for observing, understanding and modeling the phenomena occurring at the solid/liquid interface which control the dissolution reaction. A millifluidic reactor of about 1 mL was developed for the continuous dissolution of millimeter or submillimeter solid particles in a nitric acid stream. New experimental and analytical monitoring techniques were used (observation at the interface by confocal microscopy and epifluorescence, tracking of the species involved, pH monitoring at the interface by fluorometry). Qualification and experimental implementation of these techniques were first conducted on a nonradioactive surrogate, copper. These observations were used to better understand and quantify continuously and *in situ* the material dissolution mechanisms and the pH variation at the interface, as well as providing data on the behavior of the off-gases. Intermediate species favorable to the reaction were identified, and made it possible to quantify the coupling between hydrodynamics and dissolution kinetics. We were also able to obtain a pH map of the reaction interface, which is very difficult to implement for this type of reaction in corrosive media.

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1. Introduction

An important step in existing industrial recycling processes for spent nuclear fuel, after cutting up the spent fuel assemblies, is the selective dissolution of uranium oxide in a continuous dissolver containing concentrated nitric acid. The dissolver operation is complex. A dissolution model should help to have a better knowledge of chemical engineering problems related to the process. The model must be representative of the phenomena involved during the dissolution reaction.

This oxidizing reaction involving three phases is not well known, however, because of the complexity of the phenomena governing each phase. On the one hand, because of the multiplicity and instability of the species derived from nitric acid that can be present under the experimental conditions, the composition of the liquid phase is complex and difficult to analyze. Many authors have specu-

lated that some of these species are probably autocatalytic. Among them, Taylor et al. [1] and Herrmann [2] showed that increasing the stirring speed in a batch reactor decreased the dissolution rate. They postulated that stirring and the resulting shear rate caused diffusion of the autocatalytic species formed far from the liquid/solid interface. Although nitrous acid is often mentioned as the main autocatalytic species, the exact nature of the species involved must still be identified. On the other hand, the composition of the gas phase is difficult to determine because it is constantly changing due to the chemical equilibria involved in nitric acid media. Sakurai and Takahashi [3], for example, determined that the principal gases present at equilibrium are nitrogen monoxide (NO) and nitrogen dioxide (NO₂), which are at equilibrium with nitrous acid.

The microstructure of the solid also impacts the dissolution rate: the reaction does not occur uniformly on the surface of the solid, which is subject to change throughout reaction. Finally, the numerous gas bubbles formed at the solid surface during dissolution probably also have a major role.

For all these reasons, the available models based on phenomena limiting the surface reaction or the transport of species to and from

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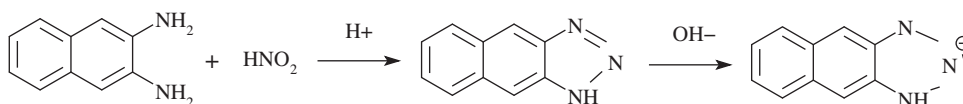


Fig. 1. The reaction between DAN and nitrous acid results in the formation of naphthotriazol or naphthotriazolate.

the surface are inadequate because of the many unknowns: physical constitution and chemical composition of the surface, transport phenomena affected by the presence and release of bubbles, etc. Our investigations seek to obtain the additional data by evaluating the concentrations of species at the interface.

The reactors of a few hundred milliliters classically used in such studies can only provide “macroscopic” kinetic data that in fact correspond to many superimposed phenomena occurring at microscopic scale at the reaction interface. New tools must therefore be developed for *in situ* monitoring at smaller scale of the overall behavior and of variations in the concentration of the species present. The observations and kinetic data acquired will be used to develop and provide data to a dissolution model taking into account the combined effects of mass transfer, kinetics, and the presence of dissolution off-gases. Only the exploratory experimental part of our work is described here; no aspects of modeling will be discussed.

To eliminate the constraints arising from work in a radioactive zone, the method was developed without nuclear material, using a nonradioactive surrogate for uranium dioxide. A study by Kobayashi and Uchida [4] established a parallel between the dissolution of copper and uranium dioxide in nitric acid at moderate temperature (30 °C). The dissolution mechanism would also involve nitrous acid as an autocatalytic species. For the purposes of this study, copper was also chosen to develop the techniques used. The objective was not to find a surrogate capable of exactly reproducing the same behavior as uranium dioxide, but rather to recreate the dissolution products obtained under various conditions and to observe their behavior, while perfecting a technique suitable for measuring their concentration. The results presented here concern the observation of phenomena occurring at the interface involving chemical species including H_3O^+ (with pH monitoring) and nitrous acid, and our understanding of the precise role of the dissolution off-gases.

2. Materials and methods

Copper was procured from Goodfellow in the form of spheres 1 mm in diameter.

2.1. Experimental setup

2.1.1. Objectives

The experimental setup was designed to allow *in situ* monitoring of the species involved in the dissolution. Miniaturization of the equipment was therefore indispensable to allow microscopic observation at the solid/liquid interface where the reaction takes place. A millifluidic reactor was developed for this purpose. A reactor of this size appreciably reduces the volume of waste produced, which is a significant advantage in the nuclear field.

2.1.2. Description

The device used in the laboratory is shown schematically in Fig. 2. Nitric acid is injected into the millifluidic device by a Fisher Scientific push–pull syringe pump.

The device, shown in Fig. 3, is designed to observe the dissolution of a sphere with a microscope through a quartz window. It is made of polydimethylsiloxane (PDMS). The geometry of the dissolution tank was optimized to minimize dead volumes. The solid to be dissolved is held securely by a metal tube machined at the end,

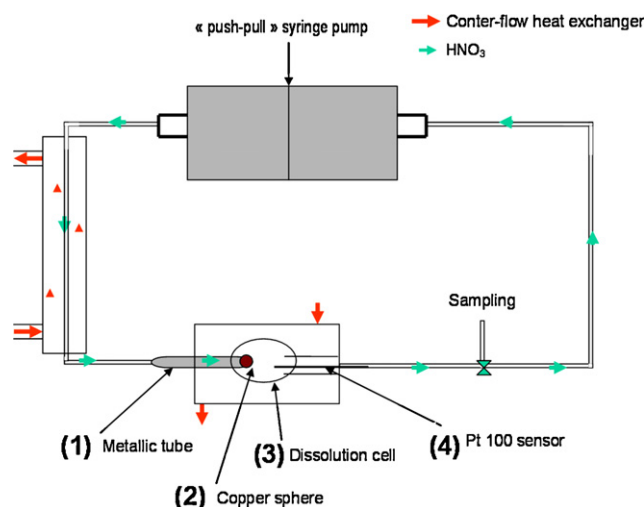


Fig. 2. Detailed diagram of test setup.

placed at the entrance of a reactor with a volume of about 1 mL. The metal tube is also used to supply nitric acid for optimum attack of the solid.

The millifluidic device includes an integral heat exchanger designed with two metal tubes on each side of the reactor, in which water flows parallel to the countercurrent flow of nitric acid. To allow operation at temperatures above 40 °C, the nitric acid is pre-heated by a coaxial heat exchanger with countercurrent water flow. The temperature is measured in real time in the dissolution cell using a Pt 100 sensor.

2.2. *In situ* pH monitoring

2.2.1. Principle

Fluorescent probes are widely used, particularly in cell biology to measure the pH and intra- and extracellular pH gradients (Bright and Fisher [5]; Martin and Jain [6]). Fluorescent pH probes are generally used in the pH range around the ground state pK_a . The absorption and emission spectra are therefore pH-dependent in the range investigated.

In highly concentrated nitric acid media, as for spent nuclear fuel dissolution, the fluorescence of many common pH-sensitive fluorophores is inhibited, making them unusable. The purpose of

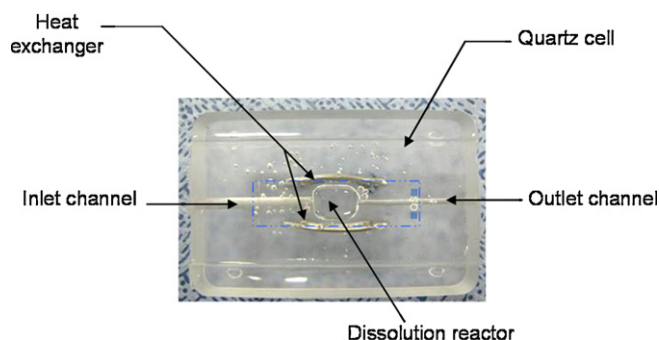


Fig. 3. Millifluidic device.

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