



# Photocatalytically driven dissolution of macroscopic nickel surfaces

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## ABSTRACT

Photocatalytically generated H<sub>2</sub>O<sub>2</sub>-driven nickel dissolution has been studied as a novel, secondary waste minimal decontamination process for nuclear process steels. Nickel corrosion experiments in dilute H<sub>2</sub>SO<sub>4</sub> show that at deliberately added [H<sub>2</sub>O<sub>2</sub>] ≤ 1 mM, nickel dissolution occurs *via* formation and dissolution of NiOH groups; at [H<sub>2</sub>O<sub>2</sub>] ≥ 10 mM (pseudo-)passivation by NiO prevents this. Furthermore, Nickel also dissolves slowly in mild acid, dissolution that is significantly accelerated in the presence of photogenerated peroxide – suggesting that photocatalytically generated H<sub>2</sub>O<sub>2</sub> could be used to selectively increase dissolution of Ni, and potentially steel, surfaces that normally dissolve only slowly in mild acid.

## 1. Introduction

Stainless steels are ubiquitous on nuclear sites either as construction materials or as the primary fabric of process plant components such as pipework, vessels, waste storage tanks, *etc.* In the case of the latter radioactive contamination, originating from the ‘plate-out’ of radioactive solids, colloids or metal ions onto stainless steel surfaces in plant vessels, tanks, pipes *etc.*, is a universal problem across nuclear licensed sites. As a result, improved chemical decontamination techniques to either reduce radioactivity levels to enable man access for ‘hands-on’ decontamination and/or to allow for waste to be reclassified to a lower level are required.

Decontamination techniques for the removal of fixed (*i.e.* chemically bound) contamination from metal surfaces are mostly redox chemistry based and involve either: (1) simple one step treatments such as the cerium oxidant based MEDOC process (Metal Decontamination by Oxidation with Cerium) [1–6] or high temperature citric acid wash [7], or (2) more complex multistep processes, such as the permanganate oxidant based CORD process (Chemical Oxidising Reduction Decontamination) [8–12]. Importantly, hydrogen peroxide in combination with actinide/transition metal complexants such as hydroxycarboxylic acids [2] or carbonates in the COL process (Carbonate-based Oxidative Leaching) [13–15], has proved to be a useful single step decontamination process that produces less secondary waste. However, the disadvantages of these chemical wash techniques are difficulties in accessing some parts of old plants (*e.g.* pipe junctions), the generation of large arisings of acidic secondary effluents (MEDOC and CORD) and often a need to use decontamination agents which are themselves

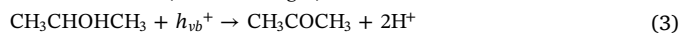
incompatible with existing effluent and waste treatment processes. Therefore there is real benefit if alternative decontamination processes can be identified which offer advantages in improving access to some areas of plant and/or do not ablate non-active surfaces and/or use more benign reagents. Photocatalytic promotion of H<sub>2</sub>O<sub>2</sub>-based advanced oxidation processes (AOPs) may provide such an alternative decontamination option.

Photocatalysis can be loosely defined as the promotion of a reaction by the photoexcitation of a catalyst. The primary step of photocatalysis involves the absorption of light by a solid substrate immersed in a liquid, typically aqueous, medium to create electron hole pairs which in turn generate free radicals such as OH· or molecular species such as H<sub>2</sub>O<sub>2</sub> able to drive secondary reactions. Common applications include, *inter alia*, the driving of AOPs [16–19], precious metal recovery [20,21], and the removal of heavy elements from effluent streams [22–24]. Common photocatalysts, usually deployed in particulate form, include cadmium sulphide and the oxides of tin, tungsten and titanium, with TiO<sub>2</sub> the most prevalently used [25–27].

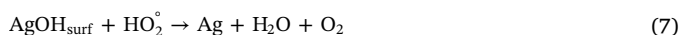
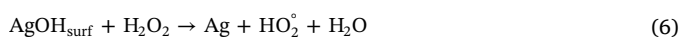
Of relevance to steel decontamination technologies is the recently reported photocatalytically driven, hydrogen peroxide mediated, dissolution of macroscopic silver surfaces by a one electron oxidation process, Ag to Ag<sup>+</sup> [28]. Using a colloidal TiO<sub>2</sub> dispersion, hydrogen peroxide is photocatalytically generated *via* the conduction band electron driven reduction of molecular oxygen with scavenging of valence band holes provided by additional propan-2-ol in order to avoid electron/hole recombination as follows [29]:

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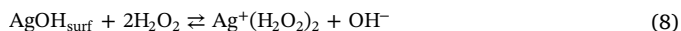
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*Photocatalytic Excitation**Formation of Hydrogen Peroxide**Electron Donor (Hole Scavenger) Oxidation*

In the presence of a silver surface, hydrogen peroxide undergoes a heterogeneous catalytic process decomposing to water and oxygen via the generation of a surface silver hydroxide [30,31]:



During the decomposition of  $\text{H}_2\text{O}_2$  dissolution of silver occurs as a side reaction,



the extent of this reaction being small compared to the main decomposition of hydrogen peroxide.

Furthermore, this photoinduced dissolution effect is both highly controllable (switchable through application/removal of light) and spatially specific (differential dissolution rates observed from directly and partially illuminated surfaces and negligible dissolution observed from un-illuminated systems). This suggests that photocatalytically driven metal dissolution could potentially be developed into a new spatially specific, and thus secondary waste minimal, metal surface decontamination technique.

Additional advantages may accrue, especially from the potential for maximising peroxide decontamination efficiency, by photogenerating  $\text{H}_2\text{O}_2$  *in situ* and directly adjacent to the site of contamination. As such, the severity of other components in the decontamination reagent could be reduced – including reagent acidity, a move that would be advantageous in reducing indiscriminate attack on metal surfaces during deployment (a problem with strong mineral acid-based decontamination techniques such as MEDOC) and so further reducing secondary waste arisings.

Thus, within the context of further development of photocatalytically driven metal dissolution as a decontamination technique, this paper applies this process to a more commonly encountered metal surface, nickel. While the corrosion resistance of stainless steel is predominantly provided by thin iron and chromium passive oxide layers formed in response to oxidative attack, a high weight percentage of nickel is also present in 304L and 316L (low carbon) nuclear process stainless steels [32] and in steels used in fuel cladding of UK design advanced gas cooled reactors (AGR). Addition of nickel increases oxidative resistance at neutral to alkaline pHs by widening the window of passivity and the region of immunity of stainless steels, providing improved corrosion resistance in reducing environments [33]. Nickel also increases the crystal phase stability of nuclear process steels, improving mechanical properties such as ductility, toughness and weldability [34]. As such, selective dissolution of nickel may potentially disrupt the steel surface structure through grain boundary corrosion and Ferritization, releasing adhered radionuclide contaminants.

This study is therefore novel in that it presents the first investigation of the photocatalytically-driven dissolution of a metal: (i) that is oxidised via a potentially slow 2 electron transfer process; (ii) that, for much of the water  $E_{\text{h}}$ -pH stability region, is protected against dissolution by a passivating surface layer of nickel oxide/oxyhydroxide; and (iii) is a major component of alloys that are widely used for structural and process applications – thus opening the possibility of using this

technology for industrially relevant decontamination and clean-up applications. This is in contrast with the earlier work performed on silver [28], a metal that is not subject to any kinetic limitations in its one electron oxidation to form  $\text{Ag}^+$ , does not passivate and thus is limited to predominantly ornamental uses.

While the effect of sulphuric acid on nickel dissolution [35–40] and conversely the rate of hydrogen peroxide decomposition over nickel catalysts [41–45] has been well characterised, there have been relatively few studies on the effect of deliberately added hydrogen peroxide on the rate of Ni dissolution in mild acid (pH 2 and above) solutions such as those suggested above. Schumb et al. report that in the presence of both high molarity hydrochloric and sulphuric acids, hydrogen peroxide is capable of dissolving metallic nickel [46]. However, in neutral and alkaline conditions, nickel shows significant resistance to hydrogen peroxide corrosion. Thus, before attempting photocatalytically driven, hydrogen peroxide mediated, dissolution of nickel, we first characterise by potentiometry and quartz crystal microgravimetry the behaviour of nickel electrodes in mildly acidic (pH 2.1  $\text{H}_2\text{SO}_4$ ) hydrogen peroxide solutions of increasing concentration via the electrochemical quartz crystal microbalance (QCM). As demonstrated in our previous publications [28,47], the capacity of the QCM to measure nanogram changes in the mass of metal electrodes in real time makes it especially suitable for *in situ*, measurements of corrosion and dissolution of the type that may be expected in the nickel system studied here.

## 2. Experimental section

### 2.1. Materials

All chemicals were of AnalaR grade or better and supplied by Sigma Aldrich (Gillingham, Dorset, UK) with the exception of 35 wt.% hydrogen peroxide supplied by Fisher Scientific Inc (Loughborough, Leicestershire, UK) and Degussa P25 Titanium Dioxide supplied by Evonik Industries (Rellinghauser Straße 1–11, Essen, Germany).

All  $\text{H}_2\text{O}$  used was doubly distilled water from a home-made still, further purified by a deionisation system (E-pure model 04642, Barnstead/Thermodyne, Dubuque, Iowa, USA) to a resistivity of  $1.8 \times 10^5 \Omega\text{m}$  and a pH of 6.7.

Except where explicitly stated, all experiments were conducted in Pyrex® glassware due to its transparency to wavelengths down to 300 nm.

### 2.2. Quartz crystal microbalance piezoelectrode preparation

QCM piezoelectrodes comprised of polished Ni coated quartz crystals with a Cr adhesion layer (front and rear) were supplied from Testbourne Ltd. (Hassocks Wood, Basingstoke, Hampshire, UK). The crystals were AT cut quartz, with a nominal resonant frequency of 5 MHz. All crystals were solvent washed prior to use by successive washes of chloroform, acetone and finally ethanol to remove any surface contaminants.

### 2.3. Microgravimetric studies of Ni dissolution in the presence of deliberately added $\text{H}_2\text{O}_2$

Mass changes at the QCM piezoelectrode surface, due either to material dissolution or deposition, can be taken to be directly proportional to the resultant resonant frequency change if it is assumed that the associated mass is rigidly bound to the electrode surface. This relationship is commonly expressed through the Sauerbrey equation [48]:

$$\Delta f = -C_f \Delta m \quad (9)$$

where  $C_f$  is the mass sensitivity of the 5 MHz AT-cut crystal. The value of  $C_f$  was calibrated by the electrochemical deposition and dissolution of copper via cyclic voltammetry [49,50] and was found to be  $0.0557 \text{ Hz}^{-1} \text{ ng cm}^{-2}$ , which is in excellent agreement with a

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