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Microbially induced corrosion of D9 stainless steel–zirconium metal waste form alloy under simulated geological repository environment

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ABSTRACT

Metal waste form (MWF) alloy specimens were exposed to *Bacillus* sp. and *Pseudomonas* sp. cultured in simulated Kalpakkam and Rajasthan ground water media to study the microbially induced corrosion. Total viable count and epifluorescence microscopic results showed good bacterial attachment on MWF surface. Scanning electron microscopy and atomic force microscopy studies on etched MWF surfaces showed preferential bacterial adhesion on the Zr-rich intermetallic phases. Potentiodynamic polarization experiments showed active corrosion potential and higher current density for biofilmed surface. Electrochemical impedance spectroscopic study showed passive film weakening under the biofilm. Corrosion effect of *Pseudomonas* sp. is comparatively more than *Bacillus* sp.

1. Introduction

Geological repository is a permanent disposal facility with stable geologic environment. It entail a combination of waste form, waste package, engineered seals and the geology that is suited to provide high level of long-term isolation and containment without future maintenance [1]. The purpose of deep geological repository is to provide passive protection against any harmful release of radioactive material for the future generation, even after the memory of the repository has been lost [2]. The host media for the geological repository can be sources of oxygen, water, and other microbial species that can be aggressive in altering the nature of materials used for containment of waste [3]. Biofouling is a major problem in almost all circumstances where water based liquids is in contact with some materials. For engineering structural materials, virtually all forms of microbiologically influenced corrosion (MIC) reported in literature are associated with localized corrosion underneath a biofilm [4,5].

Metallic waste generated at the end of electrometallurgical treatment of spent nuclear metallic fuel is known as metal waste form (MWF) alloy. The MWF alloy contain stainless steel (SS) cladding hulls, noble metal fission product, zirconium (Zr) from alloy fuel and the actinide elements left in the anode dissolution basket of electro-refiner. This metallic waste is consolidated by melting under argon atmosphere, packed as engineered barrier system and finally disposed to geological repository [6]. The baseline composition of MWF alloy is mainly SS–Zr alloy. However, the Zr content of MWF alloy is expected to vary from 5 to 20 wt.% [7,8]. The noble metal fission product (NMFP) content varies from 0.5 to 4 wt.% and the actinide content varies from 2 to 10 wt.% (mostly in the form of uranium) [9–11]. The role of Zr is to improve alloy properties by producing a host phase for actinide and fission product and also to lower the melting point of the alloy [11,12]. The oxide layer that forms on the surface of zirconium and its alloys is known to be chemically stable in many environments, with good mechanical strength and excellent wear and corrosion resistance [13]. However, it is also well reported that zirconium has excellent biocompatible property [13,14]. Hence, microbes present in natural water of the repository environment can favor biofilm formation on MWF alloy. Biofilms are mostly patchy in nature and will initiate concentration cells at the metal biofilm interface [15,16]. Therefore, localized corrosion can occur under the biofilm [4,15,16] and can encourage leaching out of radionuclides, which pose an environmental threat [17,18].

The aim of this present study is to monitor the microbial attachment and its effect on D9 stainless steel–zirconium [19] based MWF alloy. For this purpose we have chosen two simulated ground water media with two predominant biofilm formers, such as *Bacillus* sp. and *Pseudomonas* sp. Two approaches were used to realize the objectives. The first approach involved determining the effect of biocompatibility of zirconium in MWF alloy on microbial adhesion. The second is to study the effect of microbially induced corrosion using electrochemical techniques. The geological repository environment selected was simulated Rajasthan ground water near Thar Desert, Jaipur city, Rajasthan, India and simulated Kalpakkam ground water at Kalpakkam, India [20,21].

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2. Materials and methods

2.1. Specimen preparation

The MWF alloy required for this study was prepared as an ingot of alloy D9 stainless steel [22] with zirconium by using vacuum arc melting furnace (Button Pancake Melting Furnace, Microtorr Vacuum Systems Pvt. Ltd., India). The alloy was melted three times for better homogeneity at applied potential 20–28 V and 600–900 A current in vacuum chamber which evacuated and refilled with high purity Ar of about 400 mm Hg (0.53 atm). The melt was allowed to cool inside the furnace to obtain pan cake shaped cast form. Table 1 shows the chemical composition of the MWF alloy analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES).

The ingot was cut into several pieces of $10 \times 10 \times 5$ mm dimension. Different specimen preparation techniques have been employed for different experiments and the detailed specimen preparation procedures are given below.

(a) The specimens used for monitoring corrosion using electrochemical techniques were mounted in an epoxy resin with a brass rod for electrical connection. The exposed surface of the mounted specimens were abraded to 1200 grit SiC emery paper and then polished up to 1 μm diamond finish. The edges of the specimens were covered with corrosion resistant lacquer to prevent crevice attack at the specimen–mount interface.
(b) The specimens used for monitoring microbial attachment by bacterial density count and epifluorescence microscopic studies were mechanically abraded to 1200 grit SiC emery paper on all the sides.
(c) For scanning electron microscopic (SEM) and atomic force microscopic (AFM) studies the specimens were polished up to 1 μm diamond finish and electrochemically etched in 10 wt.% ammonium per sulfate solution for an applied potential of 1.8 V for 1 min.

Prior to exposure of the specimens to the respective culture media, all the specimens were ultrasonically cleaned using soap solution followed by acetone and exposed in UV light for 15 min for sterilization.

Table 1
Chemical composition of MWF alloy.

Elements	Fe	Cr	Ni	Zr	Mo	Si	Ti
wt.%	65.5	11.8	12.8	8.5	0.7	0.5	0.2

2.2. Test Organisms

Microbial adhesion on MWF alloy was evaluated using a gram-negative bacterium, *Pseudomonas* sp., and a gram-positive bacterium, *Bacillus* sp. The reason for the selection of the above genera was that they were identified as major colonizers of the biofilms formed in a fresh water reservoir at Kalpakkam, India [23,24]. Characterization and identification of the bacteria up to genus level was carried out based on morphological, physiological and biochemical tests (Table 2) as in Bergey's Manual of Systematic Bacteriology [25,26].

2.3. Exposure medium (ground water and microbial culture media)

The geological repository chosen for the experiments was simulated Kalpakkam ground water (KGW) medium [20] and simulated Rajasthan ground water (RGW) medium [21]. Typical compositions of KGW and RGW media are given in Table 3.

The *Bacillus* sp. and *Pseudomonas* sp. were cultured and grown for 24 h in 100 ml nutrient broth solution (sterilized by autoclaving at 120 °C for 15 min). One milliliter of this culture solution was added to 150 ml of the simulated KGW and RGW media individually and allowed to grow for another 24 h. Seven MWF specimens (2 for corrosion monitoring, 2 for viable count, 1 for epifluorescence study and 2 for surface characterization by SEM and AFM) were suspended in that solution for 5 days. One weight percent of glucose was added to the medium to maintain the microbes in growing conditions. Studies in each condition were repeated thrice for reproducibility.

2.4. Post exposure studies

2.4.1. Bacterial count

The quantitative analysis of total bacterial attachment was investigated by total viable count (TVC) method [27]. The growth of bacteria in the simulated repository environment was confirmed by performing TVC analysis of the media after 5 days of exposure. For each experimental condition two specimens were used for TVC estimation. The specimens were removed from the medium, gently washed to remove loosely adhering cells and the remaining bacterial cells on the specimens were dispersed into 15 ml sterile phosphate buffer (0.0425 g KH_2PO_4 and 0.19 g $MgCl_2$ per liter) by ultrasonication. The duration for the sonication for optimum recovery of the cells was found to be 5 min [28]. Serial dilution

Table 2
Results of morphological and biochemical tests of bacterial sp. used.

Properties	*Pseudomonas* sp.	*Bacillus* sp.
Gram reaction	Gram-negative	Gram-positive
Morphology	Very small rods	Long rods
Pigments	Green fluorescent colony, pigment diffuses into media	Off white, rough spreading irregular colonies, no pigments
Motility	+	+
Catalase	+	+
Oxidase	+	+
Specific reactions		
Anaerobic glucose fermentation	+	+
Nitrate reduction	+	+
Citrate Utilization	+	+
Growth on cetrimide agar	+	–
Indole production	+	–

+, Present; –, absent.