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Technical note

Corrosion behaviour of four handguns in aqueous environments: Corrosion product characterization and effects on estimating the time since deposition

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ABSTRACT

When a firearm has been disposed of in a body of water and becomes corroded, its appearance is altered and determining a time-since-immersion may be of import to the investigation. Therefore, in this study, the corrosion and mass loss of four handgun slides over a period of 180 days were examined. Solid-state characterization of the metals and their corrosion products via SEM/EDX and powder X-ray Diffraction (pXRD) was performed. The pXRDs were analyzed against the NIST Powder Diffraction Database to determine the crystalline phases. Filings from the SS416 standard, Llama and Ruger handgun slide predominantly consisted of iron alloys. After 180-days in solution, pXRD indicated that the adherent corrosion products consisted of 1) γ-FeOOH and 2) iron oxide (Fe_3O_4 or Fe_2O_3). Additionally, pXRD analysis indicated that the adherent corrosion products of the SS416 standard also consisted of CrO_3. Metal filings from the Raven and Jennings handgun slides were a mixture of iron–nickel–zinc and EDX and pXRD analyses of the corrosion products, when submersed in deionized water, indicated that the products consisted of: 1) γ-FeOOH, 2) iron oxide (Fe_3O_4 or Fe_2O_3), and 3) $ZnFe_2O_4$ or ZnO; where the Jennings adherent rust contained $ZnFe_2O_4$ and the Raven adherent rust contained ZnO. Further, pXRD of the corrosion products from these alloys, when submersed in 25 PSU (Practical Salinity Unit) solution, indicated that the products consisted of: 1) ZnO, 2) $Zn(OH)_2$, 3) α-$Ni(OH)_2$, and 4) NaCl.

The data thus indicated that both metal composition and the presence of chloride ions had significant impacts on rates and products of corrosion and suggest that the presence of Cl^- changes not only the rate of corrosion, but also the corroding species itself. While mechanisms and rates of the chloride driven corrosion processes offer explanations as to the different oxides and hydroxides observed between immersion conditions, they do not offer an explanation for the differences observed between handguns. Therefore, utilizing a general approach where surface area coverage of corrosion products is the sole consideration is not sufficient to determine time-since-immersion. Attempts to determine a time-since-immersion would require *a* priori knowledge of the mechanism of corrosion for a given metal mixture within a specified environment. The results described herein give indications as to the possible corrosion mechanism driving the process in high and low Cl^- environments and show the necessity of including the metal composition, rust composition and ion concentration in any models that attempt to elucidate the time-since-immersion of handguns for forensic applications.

1. Introduction

Physical examination of evidence retrieved from crime scenes is an important component in crime scene analysis and forensic investigations. Evidence is typically classified into 3 types: biological, chemical or trace. Each type of item collected requires its own procedure for analysis within a specific unit of a forensic laboratory. Firearms, bullets and gunshot residue are typically examined in the ballistics unit, where the examination of firearms normally includes examination of class characteristics and/or serial number identification.

Although the solid-state characterization of guns or their corrosion products is not commonplace, there have previously been efforts to utilize the intrinsic characteristics associated with metallic objects and their corrosion within forensic applications. If the time since deposition is known, then association of a metallic object to a crime may be founded, or more importantly, may be excluded as probative to a specific case or investigation. An example of such a case is cited by Shanahan [1]. Specifically, in the cited case, a 0.22 caliber brass cartridge case was found at the scene of a double murder 18 weeks after the crime occurred. At the time of the investigation the prosecution assumed that the cartridge case found at the scene was relevant to the investigation and related to the crime. However, the defense argued that the cartridge case was not pertinent to the said case and contended that the cartridge cases on exhibit were not in the soil for the 18 week period and were deposited at a later date. In response to this and other

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Table 1
The mean pH, salinity, conductance and dissolved oxygen (DO) content of the water used throughout the 180 days.

Solution	pH	Salinity (PSU)	Conductance (mS/cm)	DO (mg/L) Min−max
0 PSU	7.5 ± 1.4	0.01 ± 0.03	0.03 ± 0.06	8–11
25 PSU	6.1 ± 1.3	25.9 ± 1.2	37.8 ± 2.7	7–10

Standard deviation listed as ±2SD.

cases, a field study was conducted by Shanahan [1] and showed significant differences in color among the corrosion products. Additionally, the level of corrosion, as assessed by the amount of 'rust' present on the surface of the cartridges, significantly differed. No attempt was made to characterize the corrosion products and no explanation as to the origins of the variability was offered. As a result, it was concluded that qualitative assessments of corrosion via visual inspections of the surface did not result in reliable forensic information and should not be presented as a means to approximate the time since deposition.

Since Shanahan's 1977 publication, the study of material corrosion in various environments has evolved and a significant body of work which characterizes the effects of the environment on the corrosion process has become available. For example, when studying the mass loss of mild steel in high-temperature hard fresh water, Melchers et al. showed a linear relationship between the mass-loss and level of dissolved oxygen. However, the linearity was maintained only within a 0.5 year time interval. At times greater than 0.5 years, corrosion was controlled by mass transport or the ability of the oxygen to diffuse through the newly formed oxide layer [2]. Malik et al. have revealed a positive linear relationship between the increase in corrosion rate of a variety of commercial grade stainless steels and temperatures up to 65 °C. After 65 °C, the increased solubility of oxygen caused a decrease in the oxygen concentration resulting in a stabilization of the corrosion potential [3]. Graedel conducted corrosion studies of zinc exposed to the atmosphere, characterized the products that formed and determined that the pH of the surface of the metal was crucial to the mechanism of dissolution, and suggested that pH specifically affected the dissolution of the passive oxyhydroxide surface of zinc [4]. Similarly, Mouanga et al. determined the mechanism of corrosion and the expected corrosion products of zinc were affected by pH and chloride concentration and suggested that the likely corrosion products of zinc were 1) ZnO and $Zn(OH)_2$ in alkaline environments and 2) ZnO, $Zn(OH)_2$, and $Zn_5(OH)_8Cl_2 \cdot H_2O$ in chlorinated acidic environments [5].

The composition of the metal is also known to directly impact the rate of corrosion and the effects of metal composition on corrosion rate have been extensively studied. For example, it has previously been shown that the level of Cr in iron based metals can affect the formation of rusts and their respective crystallite sizes [6,7]. Other additives, such as Mn, Cu, Ni, Ti and Zn have also been shown to affect the corrosion mechanism and resultant products [6,8,9].

Given the recent advances in solid state characterization and classification of environmental impacts on corrosion, methods aimed at predicting corrosion rates and wastage based on empirical and physical models have also been explored. For example, Paik et al. recently published a method for the development of an empirical model to predict time-dependent corrosion wastage for seawater ballast tank structures of aged ships [10], while Melchers et al. and Kihira et al. have provided corrosion models that allow for environmental factors [11,12]. In each case, knowledge of either the initial mass, metal composition and/or environment was known or approximated.

In many instances, forensic investigations require either estimates of the time-since-immersion or detailed studies that provide evidence to suggest why the determination is prone to error. In the case of metals retrieved from aqueous environments, the items retrieved may be from unknown sources and have unidentified metal compositions. Therefore, it is of interest to determine whether estimates of time-since-immersion may be procured from certain 'classes' of handguns or from handguns with similar compositions within a specified environment.

Given the developments in corrosion chemistry, material characterization, and the need of the forensic science community, it was of interest to determine whether the corrosion processes of guns can be defined such that a time of deposition could be estimated via a generalized approach. This work represents a detailed study into the solid-state characterization of corrosion products of a stainless steel control and four different handgun slides. Here we present SEM/EDX and pXRD data from both the original metal filings and adherent rust from 180-day immersion studies, to assess and compare resulting morphology, elemental and crystal composition. Mass loss data is examined in light of solid-state characterization results to review the ability to determine time since deposition of metallic items in aqueous environments using measurements of surface coverage of the rust and to assess whether corrosion products are expected for certain 'classes' of handguns.

2. Materials & methods

Stainless Steel 416 (SS416) rods and four handgun slides – Llama, Ruger, Jennings and Raven – were immersed in aqueous solutions, with and without NaCl, for a period of 180 days. All SS416 samples were cut into 1-inch long rods and all handgun slides were cut in half across the width. The Llama slide had a black colored coating prior to

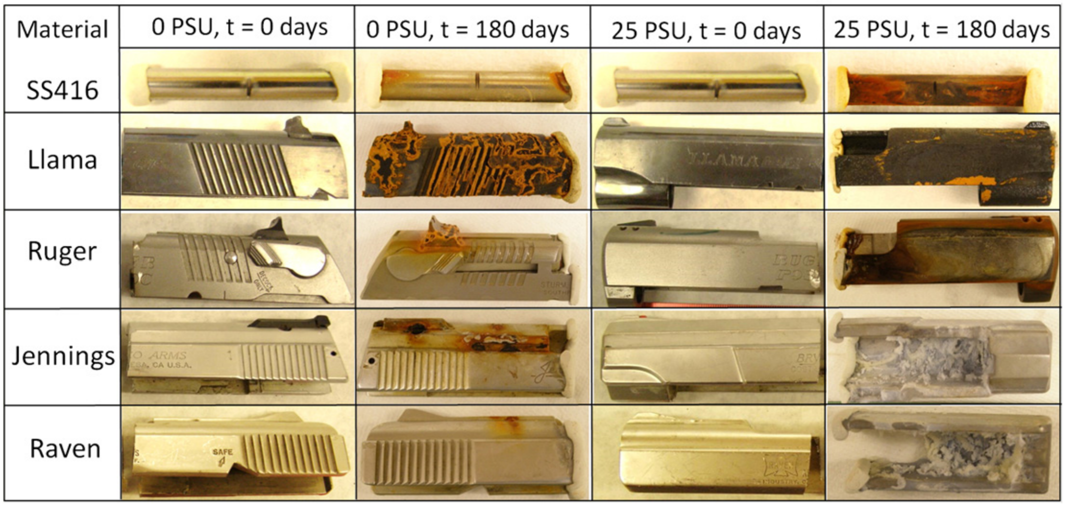

Fig. 1. Photographs of the SS416, Llama, Ruger, Jennings and Raven slides before and after submersion in 0 and 25 PSU solution for 180 days.