
AN ELECTROCHEMICAL APPROACH FOR INVESTIGATING CORROSION OF SMALL ARMS MUNITIONS IN FIRING RANGES

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ABSTRACT Corrosion of spent munitions in soil has never been previously investigated. Because of the possible environmental impact of lead leaching from bullets, this project was initiated to investigate the usefulness of electrochemical methods for measuring corrosion rates of bullets in soil. The electrolyte was soil taken from a Southern army training facility. A number of environmental conditions were simulated (rain water, acid rain, sea water, and a sea water/acid rain mixture) at moisture contents of 15% and saturation. The validity of using electrochemical techniques for measuring bullet corrosion has been established in this research. Corrosion current was observed to be very dependent on environmental conditions. The rate of corrosion was found to increase with decreasing pH and increasing chloride and moisture contents. High soil resistance and a relatively less negative value for corrosion potential were found to be associated with low corrosion rates. This is an important result since both soil resistivity and potential can be readily measured under field conditions. Additional laboratory and field studies are needed to obtain further insight into the bullet corrosion problem, including additional electrochemical tests, weight loss measurements, chemical analyses of soils, and other soil measurements.

KEYWORDS: bullets, corrosion, lead, soil, electrochemical techniques

INTRODUCTION

Over the years there have been many reports on the corrosion behavior of metals in soil. For the most part, however, these studies have been concerned with underground structures made from ferrous alloys, e.g., water mains [1], pilings [2], gas pipelines [3], and underground storage tanks [4]. Much less is known about electrochemical dissolution of nonferrous metals in soils. It appears that one corrosion problem of possibly significant environmental importance that has been overlooked in the past is that of spent small arms munitions in soil environments. For several decades at military firing ranges, used bullets have been accumulating in soils. A wide spectrum of

soil types and weathering conditions is involved. Typically military bullets consist of a lead alloy slug surrounded by a copper alloy jacket. Lead is a well-known neurotoxin [5] and causes other health problems as well [6]. Although not harmful to the degree that lead is, copper is also considered to be a toxic metal. Therefore, the release of soluble and precipitated corrosion products into soil is of potential concern, particularly regarding the possibility of their infiltration into ground water.

The literature regarding underground corrosion of lead alloys is much sparser than that pertaining to iron and steel. Studies of lead sheathing of concentric neutral

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underground telecommunication cables have been reported [7-9]. The extensive NBS soil corrosion research projects [10] utilized lead alloys for a very small percentage of the exposed specimens. Von Baeckmann [11] has reported on the cathodic corrosion of lead in soil. Booth, *et al.* [12], investigated soil characteristics that foster aggressive corrosion in a variety of nonferrous materials including lead and copper. Solid radioactive wastes are sometimes stored in underground containers made of lead, and some research has been reported regarding their corrosion behavior [13, 14]. A literature search turned up only one reference dealing with corrosion of bullets in soil [15], and none in the English language. The study of Shimodaira, *et al.* [15], investigated stress corrosion cracking behavior of brass bullets.

There are various approaches for the study of corrosion phenomena. In weight loss investigations, the specimen is exposed to the conditions of interest for a defined time period. The specimen is weighed before and after the corrosion has occurred, and the difference represents the weight lost into the environment by corrosion processes. Atoms of metal M, though, are lost from the surface by oxidation reactions such as: $M \rightarrow M^{+n} + ne^{-}$, where n is the atomic valence and e^{-} is the charge on the electron. In a macroscopic sense this means that a current flows through the metal surface. Consequently, the rate of weight loss into solution (i.e., the corrosion rate) at any given instant can be determined by measuring the current flowing through the metal/electrolyte interface. The term "electrolyte" in this context refers to the medium in which corrosion is occurring. Methods which monitor corrosion processes by determining currents and electrical potentials of the metal of interest are known as electrochemical techniques. Weight loss methods were the first ones used to study

corrosion, but in recent decades the electrochemical approach has also become a traditional means for measuring corrosion. Electrochemical methods offer the advantage over weight loss tests in that they can be carried out much more quickly. Thus they lend themselves to studies where many different environments are tested. Usually electrochemical testing has been applied to corrosion in aqueous liquid environments, although these techniques have been extended to a variety of other environments, also, such as soils. Excellent descriptions of these two approaches for studying corrosion are found in the literature [16, 17].

Few of the studies of lead corrosion mentioned above, however, used electrochemical techniques to monitor the rate of corrosion, and only one [15] could be identified which addressed small arms munitions corrosion in soils. The investigation of Shimodaira, *et al.* [15], though, did not employ electrochemical methods. The purpose of the present investigation is to study the utility and validity of the electrochemical testing approach for gauging the severity of corrosion under a range of soil conditions that might be encountered by spent bullets in the field. Ultimately it is hoped that such studies will allow determination of the soil/weathering conditions that pose the greatest hazard for lead release into soil. This should aid in guiding remediation efforts and/or future activities in the area of soil treatment to minimize corrosion of bullets.

A number of variables [1, 2, 4, 9, 12, 18, 19] have been shown to be implicated in the corrosion of metallic structures in soil, e.g., moisture content, pH, resistivity, and redox potential. Fungi have also been reported to be corrosive to lead [20]. Soil chemistry, particularly that of pore water, can also have

a substantial influence on the corrosivity of soil. Carbonates, chlorides, sulfates, and sulfides have been identified as being particularly important. The present study focuses on the importance of moisture content, pH, and chloride content on bullet corrosion. The other variables mentioned above will be examined in future investigations.

MATERIALS AND METHODS

Soil conditions

Soil for testing purposes was obtained from a southern Army training facility (SATF) which has one of the nation's largest number of firing ranges. In one series of tests, the soil moisture content was controlled to 15%. In a second series of tests, saturated soil was used corresponding to a moisture content of 24.5%. Moisture contents were verified using a Denver Instrument Co. IR-100 Moisture Analyzer. The soils were tested at room temperature and exposed to ambient atmospheric oxygen.

In this work, four different soil electrolytes were used (at the two moisture contents mentioned above) which, it was thought, would create a wide range of soil corrosivity useful for the study of the utility of electrochemical techniques. The electrolytes were a) rain water collected at Waterways Experiment Station in Vicksburg, MS, b) artificial sea water (Instant Ocean Synthetic Sea Salt, consisting of, when dissolved, 1.0249 g/kg Na, 0.04 g/kg K, 0.04 g/kg Ca, 0.126 g/kg Mg, 0.02 g/kg HCO₃, 1.85 g/kg Cl, 0.26 g/kg SO₄, and trace amounts of boron and strontium), c) simulated acid rain (made by taking rain water and adding HNO₃ to adjust pH down to 4.1), and d) a 50-50 mixture of sea water and acid rain. Firing ranges in the U.S. are found at locations that represent virtually all climatic, geographical, and soil type conditions, so it

was considered that the range of soil conditions studied here would be representative of some portion of these. Additionally, these conditions are a subset of those being used in a wider weight loss measurement project that we will report on in the future.

Acid rain is composed of a complex mixture of NO_x and SO_x compounds of anthropogenic and natural origin that have interacted with atmospheric water [21]. pH levels have been reported to be in the 3.9-5.5 range [21-23]. An acid rain mixture based on HNO₃ was chosen because of reports that SO_x emissions have significantly declined in the past, and this trend is expected to continue in the future [23]. This condition was incorporated into the testing program since the destructiveness of acid rain to metallic structures, such as statues and architectural trim, is well known [21-24]. It seems likely, therefore, that surface and subsurface spent ammunition also could be affected by acid precipitation.

Corrosion testing and data analysis

To perform the corrosion measurements, M-16 bullets were used. The "lead" slug is actually a lead-2 weight% antimony alloy. The jacket is made from a copper alloy. The bullets were cut in half axially, and a hole was drilled in the slug. The tip of an insulated copper wire was put in the hole that was then filled with Pb-Sn solder and insulated with silicone rubber sealant. The bullets were cleaned first in an Alconox detergent solution ultrasonically for five minutes, followed by a 10-second tap water rinse. Then another ultrasonic cleaning step for five minutes in ethanol was conducted, followed by another tap water rinse. As the final step, the specimens were rinsed in doubly distilled water for about 10 seconds and then were air dried. Four specimens

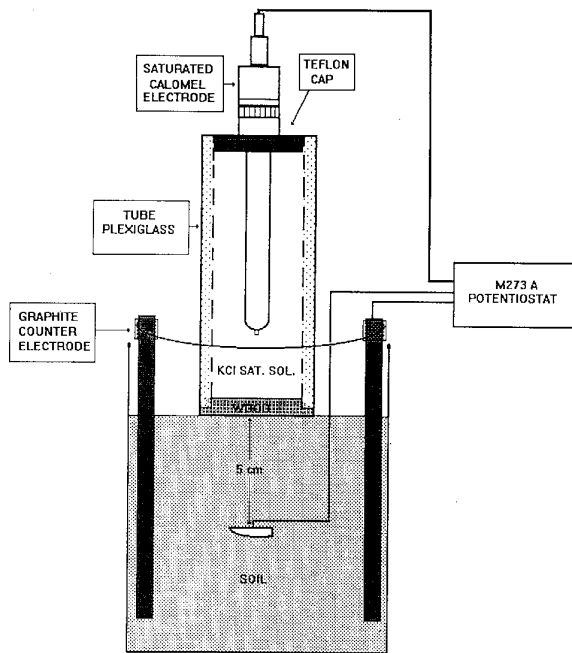


FIGURE 1. CORROSION CELL USED FOR TESTING BULLETS IN SOIL.

were tested in each of the eight moisture/soil electrolyte combinations investigated, for a total of 32 samples measured in total.

Soil with the appropriate electrolyte and moisture content was put in a two liter beaker. The bullet was buried at a depth of 5 cm beneath the surface. The corrosion behavior of the bullet was measured using electrochemical techniques. An EG&G Model 273A potentiostat operating in a computerized mode was used for this purpose. Graphite rods were used for counter electrodes. A saturated calomel electrode was used for the reference electrode. A salt bridge that consisted of a 8.25 cm diameter pine plug in a plastic tube filled with saturated KCl was employed to make electrical contact with the soil. The salt bridge design was patterned after typical Cu-CuSO₄ reference electrodes used in underground corrosion testing of ferrous

alloys [25]. A schematic of the corrosion cell is shown in Figure 1.

The experimental protocol employed for these measurements was as follows. Using the Headstart software package, free corrosion potential (E_c) was measured versus time (t) over a 1,000 second period. Over this interval, 200 data points were taken. This was done to assess the stability of the metal/soil interface. The criterion used to assess stabilization was <1 mV/minute change in potential. After stability was observed, which typically required about 1 hr of exposure, further corrosion tests were undertaken.

Since soil resistance can be very high, significant artifacts can be introduced in polarization resistance measurements if this effect (known as IR drop) is not compensated for. To measure the resistance for a given sample/electrolyte configuration, the chronoamperometric subroutine of the M270 software package was used. An 85 mV, 6 msec duration pulse was applied about E_c (taken to be the final potential observed in the E_c vs. t measurement), and the resultant current (I) was measured versus time over a 10 second period. Eighty-five mV divided by the change in current dI observed as the pulse was applied gives a measure of the soil resistance R_o . A typical measurement is shown in Figure 2. The basic theory behind such a test is as follows. The circuit analogy associated with the corroding metal system is, to a first approximation, R_o in series with a parallel RC circuit. This circuit consists of the polarization resistance, discussed following, and the capacitance of the metal/soil electrolyte interface. The capacitance is related to the structure of the double layer that is present at the metal/electrolyte interface. The double layer consists of two layers, the Helmholtz (compact) and the Gouy-Chapman (diffuse)

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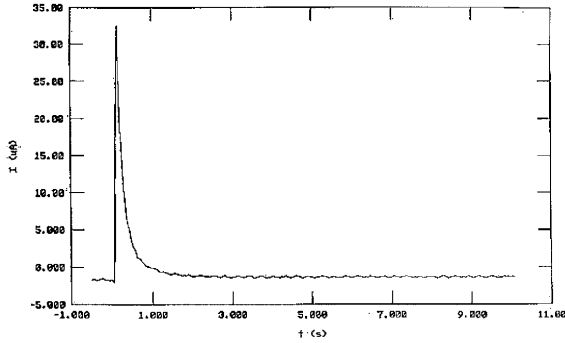


FIGURE 2. CHRONOAMPEROMETRIC MEASUREMENT USED FOR IR DROP COMPENSATION (SPECIMEN 4, SATF SOIL, 15% SEA WATER).

layers. The capacitance is related to the ionic strength of the electrolyte. The capacitance of the diffuse layer C_d is given by the following equation [26]:

$$(C_d)^2 = (DF^2/(4\pi RT)) * (\sum_i z_i c_i),$$

where D = dielectric constant of the electrolyte, F = Faraday's constant, R = gas constant, T = absolute temperature, z_i = charge on species "i," and c_i = concentration of species "i."

When a potential is quickly applied to the circuit described above, the current flows through the capacitor and R_o . Over time, though, the capacitor charges up, blocking passage of current, which then must flow through $R_p + R_o$. This results in an RC exponential decay of current versus time. The height of the current spike divided into the applied potential, as mentioned above, gives R_o . The positive feedback option of the M273A potentiostat, along with the M270 IR compensation subroutine software, allowed linear polarization and

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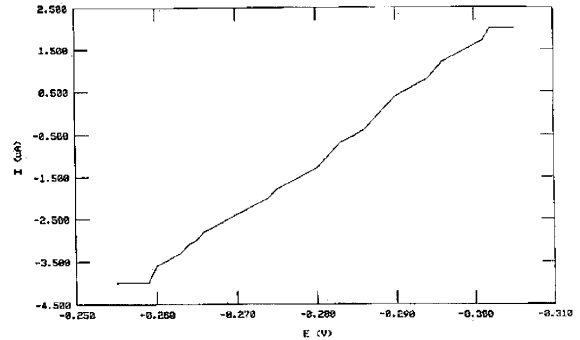


FIGURE 3. LINEAR POLARIZATION MEASUREMENT AFTER CURVE SMOOTHING (SPECIMEN 3, SATF SOIL, 15% RAIN WATER).

potentiodynamic polarization curve measurements to be conducted that were compensated for IR drop by subtracting the contribution of R_o .

Linear polarization measurements were conducted using the linear sweep voltammetry subroutine of the M270 software at a scan rate of 0.1 mV/sec in the approximate range of +/- 25 mV about the corrosion potential. Sliding average smoothing (using a ten point basis) was employed where necessary to minimize noise. Figure 3 shows a typical measurement after smoothing. The curve fit feature of the software was used to determine the slope of the E vs. I curve at $I = 0$. This slope is known as the polarization resistance, R_p . This parameter is important because according to the Stern Geary equation: $I_c = (B_a B_c) / \{ (2.3 R_p (B_a + B_c)) \}$; the corrosion current I_c (a parameter directly related to the rate of corrosion) is inversely related to the polarization resistance. The Tafel slopes B_a and B_c must be determined in a separate test, a potentiodynamic polarization curve measurement. The potentiodynamic polarization curve was measured from about

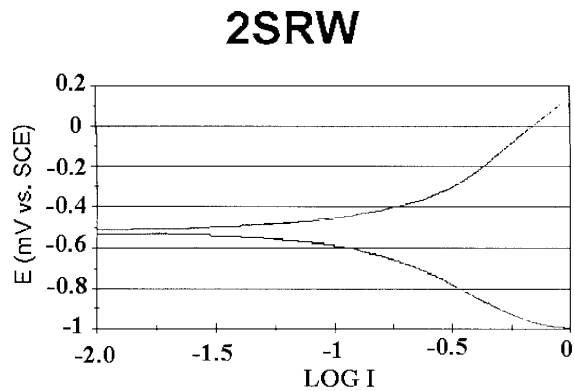


FIGURE 4. POTENTIODYNAMIC POLARIZATION CURVE, SPECIMEN 2, SATF SOIL, SATURATED WITH RAIN WATER. (0 ON THE HORIZONTAL AXIS CORRESPONDS TO 1 mA.)

600 mV cathodic to E_c to 600 mV above E_c . A typical measurement is shown in Figure 4. The Tafel constants are the slopes of the potential vs. $\log |I|$ curve in the regions where there is a linear relationship between these two parameters. B_a and B_c are the slopes of the anodic and cathodic regions of the curve, i.e., the potential regions above and below E_c , respectively. The Tafel slopes in this investigation were determined by exporting the M270 data to Quattro Pro for Windows, and using the linear regression capability of this software program.

Three measures of corrosion potential were used to compute an average value of E_c . These were 1) the range of potential observed in the E_c vs. t measurement (or in the final test, if more than one such test was conducted), 2) the potential where the current was zero in the linear polarization test, and 3) the potential of the low current spike observed in the potentiodynamic polarization curve. The extreme points of the potential range of the three measurements above were averaged to obtain a measure of the mean corrosion potential over the measurement interval. Corrosion rates were also determined in three ways: 1) the linear

CORROSION CURRENT

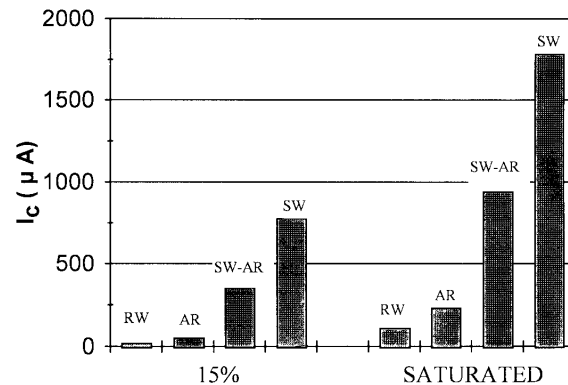


FIGURE 5. CORROSION CURRENT I_c OF BULLETS IN SATF SOIL AT 15% AND SATURATED MOISTURE CONTENTS FOR VARIOUS ELECTROLYTES (RW = RAIN WATER, AR = ACID RAIN, SW = SEA WATER, SW-AR = SEA WATER/ACID RAIN MIXTURE).

polarization/Stern Geary equation method mentioned previously, 2) anodic Tafel extrapolation, and 3) cathodic Tafel extrapolation. In the Tafel extrapolation method, the linear Tafel regions of the potentiodynamic polarization curve (mentioned above) are extrapolated back to E_c . The current at this point is the corrosion current I_c .

RESULTS

As mentioned above, the parameters measured in this investigation were corrosion potential E_c , corrosion current I_c , soil resistance R_o , and the anodic and cathodic Tafel slopes B_a and B_c respectively. The average values of the four measurements of I_c under the eight soil conditions investigated are shown in Figure 5, which displays the data at the two moisture contents in the order of expected corrosivity, i.e., from lowest to highest: rain water (RW), acid rain (AR), sea water/acid rain (SW-AR), and sea water (SW).

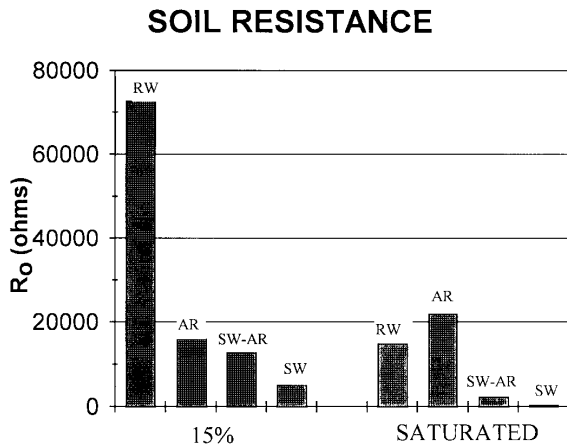


FIGURE 6. OHMIC RESISTANCE, R_o , OF SATF SOIL AT 15% AND SATURATED MOISTURE CONTENTS FOR VARIOUS ELECTROLYTES (RW = RAIN WATER, AR = ACID RAIN, SW = SEA WATER, SW-AR = SEA WATER/ACID RAIN MIXTURE).

Figure 6 presents the soil resistance data in the same format employed for I_c . It was noted that the corrosion current appeared to be inversely related with soil resistance. To demonstrate this point more clearly, I_c is plotted versus R_o in Figure 7. Figure 8 shows the corrosion potential measurements at the 15% and saturated moisture contents. Comparing Figures 6 and 8, it appeared that there might be a relation between E_c and I_c , also. To examine this possibility, corrosion current is plotted versus free corrosion potential in Figure 9.

DISCUSSION

Figure 5 demonstrates that the electrochemically-measured corrosion current I_c provides a ranking of the rate of corrosion that corresponds to the expected severity of the environmental conditions imposed. In both the 15% and saturated moisture environments, from lowest to highest corrosion rate, the ranking was rain water, acid rain, sea water/acid rain, sea water. A considerable range of corrosion

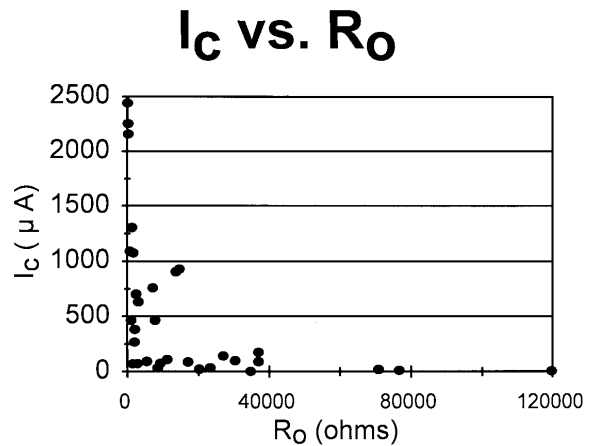


FIGURE 7. CORROSION CURRENT, I_c , OF BULLETS IN SATF SOIL VERSUS OHMIC RESISTANCE, R_o , FOR VARIOUS SOIL ELECTROLYTES AND MOISTURE CONTENTS.

current was observed in these tests—over 1,500 microamps—indicating that the test objective to span a wide range of soil corrosivities was met.

From these measurements it is clear that the most influential variable affecting the corrosion of bullets in soil, of the ones tested in this project, is the chloride content. This would suggest that the ionic strength of the pore water could play an important role for bullet corrosion. The lowered pH due to acid rain compared to rain water does have a substantial effect and more than doubles the rate of corrosion. The sea water environment, though, created a corrosion current almost an order of magnitude greater than the acid rain. The sea water/acid rain mixture was about half as corrosive as the sea water alone, as might be expected from the 50% dilution factor. As Figure 5 shows, the moisture content is a significant factor, also, as would be expected. I_c of the saturated compared to 15% moisture condition was at least doubled for all the soil electrolytes examined.

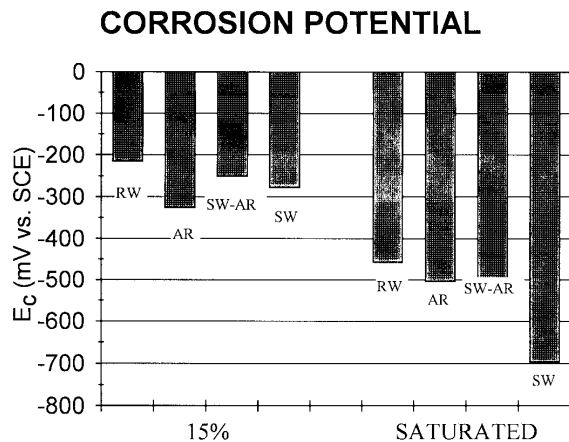


FIGURE 8. CORROSION POTENTIAL, E_c , OF BULLETS IN SATF SOIL AT 15% AND SATURATED MOISTURE CONTENTS FOR VARIOUS ELECTROLYTES (RW = RAIN WATER, AR = ACID RAIN, SW = SEA WATER, SW-AR = SEA WATER/ACID RAIN MIXTURE, SCE = SATURATED CALOMEL ELECTRODE).

The soil electrical resistance would be expected to decline as the concentration of dissolved substances increased, due to the increasing contribution of the salts to environmental conductivity. This pattern was observed for the 15% moisture content (see Figure 6). From most resistance to least resistance, the soil electrolytes ranked rain water, acid rain, sea water/acid rain, and sea water. Under saturated conditions, this same pattern was basically repeated, although the acid rain environment was anomalously higher than the rain water. This could possibly be due to random variations resulting from the relatively small number of measurements conducted here. Perhaps, too, in some cases, the contact with the soil along the surface of the graphite counter electrodes was poor in some of the tests with an acid rain environment, leading to higher resistance. Figure 6 shows that, except for the anomaly mentioned above, as the soil becomes more moist, its resistance drops precipitously.

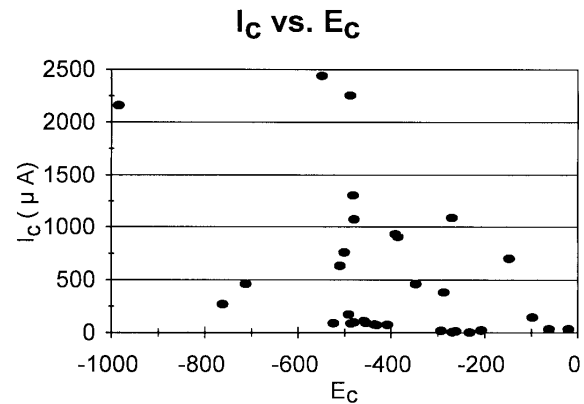


FIGURE 9. CORROSION CURRENT, I_c , VERSUS CORROSION POTENTIAL, E_c , FOR VARIOUS SOIL ELECTROLYTES. (NOTE THAT THE PREPONDERANCE OF I_c POINTS $> 250 \mu A$ LIE BELOW -250 mV SCE [SATURATED CALOMEL ELECTRODE]).

Since some of the same variables that decrease soil resistance increase I_c , the relation between R_o and I_c is of interest. It is well known that for steel pipelines, soils of decreased resistivity are highly corrosive. Figure 7 shows the I_c values that we have measured here plotted versus the measured soil resistance values. For bullets in soil, it appears that a similar relation between I_c and R_o exists as for steel. Below about 15,000 ohms, over 70% of the I_c values exceeded 250 microamps. Of the 11 specimens in more highly resistive soils (above 15,000 ohms), not one sample had an I_c value exceeding 250 microamps. This is an important finding because it directly relates to field measurements. Soil resistivity can be readily measured under field conditions, and such measurements could serve, to a point, as a metric of the corrosivity of the soil.

Figure 8 shows that, at a given moisture content, the corrosion potentials in the various environments are similar. Also, there is not a consistent ranking of E_c between the two moisture contents, nor is there a pattern of E_c values that clearly seems related to the

corrosivity of the environment. To some degree, this is expected in that the corrosion current, I_c , is a much more direct measure of corrosion rate than E_c . In contrast, Figure 8 clearly shows that potential declines with increased moisture content. Interestingly, at 15% moisture content, E_c is within the published soil corrosion potential range (-57 to -358 mV, versus the saturated calomel reference electrode, SCE) of non-galvanically coupled copper [12]. On the other hand, at saturation, the E_c value of the bullet/jacket couple is close to where one would expect the open circuit potential of lead, -376 to -908 mV SCE [12]. In terms of mixed potential theory for galvanic couples [16], this means that, in the drier soil, E_c is cathodically controlled, and in the wetter soil it is anodically controlled.

Figure 9 shows corrosion current, I_c , plotted versus corrosion potential, E_c . Comparing this figure to Figure 7, it is clear that R_o is a better predictor of I_c than E_c is, yet there is still a weak relationship between the latter two parameters. At potentials higher than about -300 mV vs. SCE, less than 30% of the samples had an I_c value exceeding 250 microamps. Below -300 mV, on the other hand, almost 60% of the samples had I_c values greater than 250 microamps. This could also be a significant finding, in that potential is also a parameter relatively easily measured in the field.

Figures showing the Tafel slopes are omitted due to the length constraint on the manuscript, yet some comments on the results should be made. The anodic Tafel slopes ranged from about 300 to 1,800 mV/decade. No clear pattern relating B_a to environmental corrosiveness or moisture content was observed. The cathodic Tafel slopes displayed a consistent ranking at both moisture contents—from highest to lowest, acid rain, rain water, sea water, sea

water/acid rain. This ranking is not directly related to environmental corrosivity. B_c was observed to be lowered slightly as the moisture content increased. The range of B_c values observed was from about 300 to 1,000 mV/decade. The value for an aqueous electrolyte with an electrode under charge transfer control is about 30-120 mV/decade. This means that, in these soil environments, there was a mass transport limitation for the cathodic reaction. The corrosion rate was thus under diffusion control.

FUTURE RESEARCH

This research project has revealed many possible avenues for future research activities that fall into several categories: correlations between electrochemical and weight loss measurements, soil metal content analysis, soil corrosivity parameters, effects of soil chemistry on corrosion, corrosion mechanisms, field studies, and soil treatment. These are discussed following. Additionally, the experimental electrochemical testing protocol developed here should be used to study a more complete range of soil conditions.

Regarding correlations between electrochemical and weight loss measurements, chronoamperometric experiments should be conducted to test the applicability of Faraday's law to the corrosion of bullets. Faraday's law relates weight loss due to corrosion W to time t : $W = k(I_{ave})t$; where I_{ave} is the average corrosion current during the interval, and k is the electrochemical equivalent. In a chronoamperometric experiment, a programmed corrosion current is selected, and the potentiostat applies the appropriate potential to achieve the current. Since high currents on the order of 1 amp can be selected, this represents a much accelerated test compared to free corrosion. It thus

provides a rapid means of correlating electrochemical measures of corrosion with those from weight loss tests. Assuming that a good correlation is observed, the electrochemical methodology developed in this project should be used to track I_c behavior in soil over the same time intervals used in the weight loss test portion of this research.

Another issue that should be investigated is the soil loading of metals as a result of bullet corrosion. These experiments may serve two purposes. First, if the chemical analyses of the metals are conducted in such a manner as to reveal concentration gradients spatially, some insight into the rate of transport of metals away from the direct site of the bullet corrosion may be achieved, an extremely important consideration in evaluating hazards in the field created by bullet corrosion. Second, by measuring soil contents of copper, antimony, lead, etc., insight can be obtained into 1) whether galvanic effects are significant (leading to the corrosion of one alloy, presumably lead, predominating over the other) and 2) whether selective leaching is occurring. Selective leaching is the dissolution of elements from a metal in amounts greater than their composition in the bulk alloy. This will increase understanding of the corrosion mechanisms involved in bullet corrosion.

Regarding soil corrosivity parameters besides moisture content (which has been tested in this investigation), a number of other variables [1, 2, 4, 9, 12, 18, 19] have been shown to be implicated in the corrosion of metallic structures in soil, e.g., pH, resistivity, and redox potential. The results of the present investigation, where resistance of the soil rather than its resistivity has been determined, give a strong suggestion that a correlation will be found between bullet corrosion rates and soil resistivity (since the

latter can be expected to strongly depend on soil moisture and salt content). The redox potential is a measure of electron abundance. The activity of sulfate reducing bacteria (e.g., *Desulfovibrio desulfuricans*) that are known to affect the corrosion of metals in soils is redox dependent. The following soil parameters—pH, resistivity, sulfate content, and redox potential—should be measured in the soil environments used for the electrochemical testing in order to further characterize aspects of the environments that may correlate with corrosion rate. These measurements should follow applicable ASTM (American Society for Testing and Materials) standards, e.g. [27, 28], if they are available. An important motivation for this work is that all of these parameters, except sulfate content, can readily be measured in field environments.

Regarding other effects of soil chemistry on corrosion, the pore water in particular can have a substantial influence on the corrosivity of soil. To characterize pore water chemistry, pore water should be removed by centrifugation, vacuum filtration, or other suitable methods from the soil used in the electrochemical testing. The chloride, sulfide, sulfate, carbonate, and nitrate contents of the various environments of interest should be measured following standard analytical techniques. Correlations should be sought between corrosion rates and various properties of the pore water including conductivity, ionic strength, content of particular salts, and the amount of total dissolved solids.

Regarding study of corrosion mechanisms, testing using AC impedance methods, should be pursued to allow determination of the degree to which charge transfer and diffusion control are involved in the corrosion of bullets in the soil. The influence of the crevice that may exist between the

copper and lead portions of the bullet may also be ascertained. As well, the impact of galvanic corrosion on the behavior of bullets in the soil can be found.

Field surveys of the soil variables that have been found in laboratory testing to be related to bullet corrosion should be conducted. This will allow sites where bullet corrosion is most severe to be identified. To verify these predictions, metal contents of soil field samples then should be measured. Care should be taken to do such tests at firing ranges where the time history of usage of the area is known, because without such information, metal transport processes through the soil away from the bullets would be a confounding variable in interpreting the relationship between corrosion rates and metal concentration build up.

Pourbaix diagrams based on the salt contents measured above should be calculated. This may help to identify pH and chemical concentration conditions which protect against corrosion such as low ionic strength. In turn this may help in the development of methods of soil treatment to ameliorate the problems associated with bullet corrosion. The Pourbaix diagram approach has appeared promising in our initial studies [29], discussion of which has had to be omitted here due to length constraints. Investigations of chemical treatment strategies to make the soil less corrosive should be carried out. These should be based on E-pH analyses and other chemical stability and speciation considerations. In developing such strategies, the amphoteric nature of lead should be kept in mind. Metallic lead is electrochemically attacked by both acidic and basic environments [30]. Minimum attack occurs in the pH 5-10 range. Such studies should have both a laboratory simulation component and, for

promising strategies, a field testing component.

CONCLUSION

The project conducted here has been concerned with measuring the rates of corrosion of bullets in soil under a range of conditions. The utility of electrochemical techniques for this purpose has been validated. It is expected that these methods could apply to other types of munitions that could potentially cause environmental problems. Corrosion current, I_c , was found to be very sensitive to the soil environmental conditions. The corrosion rate was seen to increase as pH decreased and as moisture and chloride contents increased. The most influential of these parameters on soil corrosivity for bullets was seen to be the chloride content. I_c was also seen to be related to soil resistance and free corrosion potential. Although the deleterious effect of chloride ions on the corrosion resistance of passive metals is well known, it is also possible in the research described here that the chloride is acting as a surrogate for high ionic strength. The role of ionic strength, in itself, on the corrosion resistance of small arms munitions in soil is worthy of further investigation. High resistance and noble values of potential are associated with low rates of corrosion. Conversely, highly conductive soils and those where E_c is lower foster high rates of corrosion. These findings are important because both soil resistivity and potential can be straightforwardly measured under field conditions.

This project has spawned several recommendations for future research in various areas to give further insight into bullet corrosion and to correlate the electrochemical and weight loss measurement approaches to corrosion testing. These include both laboratory and

field experiments. The tests proposed involve corrosion measurements, soil metal content and pore water chemical analysis, measurement of soil corrosivity parameters, studies of mechanisms of bullet corrosion, and the investigation of soil treatments based upon Pourbaix diagrams and other theoretical tools. Through use of electrochemical testing techniques in association with weight loss measurements, chemical analyses of soils, and other types of soil measurements, it is hoped that further insight into the problems associated with bullet corrosion and how to prevent or minimize it can be obtained.

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