



Decoppering Gun Tubes Using Selective Electropolishing

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13. ABSTRACT (Maximum 200 words) The primary purpose of this paper is to demonstrate an alternative decoppering technique of selective electropolishing, which will enable the cleaning of copper-fouled barrels in a reasonable amount of time within a maintenance schedule. A description of the electropolishing process is elaborated upon as well as the more traditional decoppering mechanisms of Cu/Pb and Cu/Bi/Sn alloying. Metallurgical aspects of the current decoppering mechanisms are presented in the spirit of providing guidance for developing a more suitable permanent decoppering solution. Two coppered regenerative liquid propellant gun (RLPG) barrels were first star-gaged and bore-scoped to determine the baseline. Electropolishing was performed on each, after which they were star-gaged and bore-scoped to enable a comparison. Details of the process are included, and the results show that this procedure can indeed clean a copper-fouled barrel without detrimental removal of base material.				
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1. INTRODUCTION

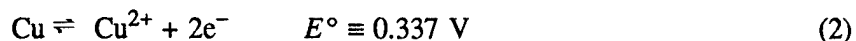
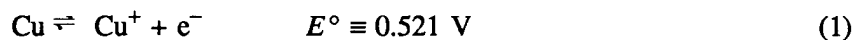
The U.S. Army must have the capability to fire the existing inventory of artillery projectiles. All of these projectiles have gilding metal (Cu-10Zn) or copper rotating bands which cause a film of copper to be deposited on the gun surface. This deposited film is not subsequently removed by the passage of the next projectiles, rather, more copper is deposited. This process can continue until the barrel can become so built up with copper that projectiles will fail to chamber (Sarmousakis 1942 and Dugway Proving Ground 1943). Even before the chambering problem arises, this copper deposit causes very deleterious effects to shot start pressure, repeatable bore resistance, peak chamber pressure, and muzzle velocity. Currently fielded systems do not have a copper buildup problem as the charges contain a lead decoppering agent (Sarmousakis 1942; Dugway Proving Ground 1943; and Robertson 1975). Lead is no longer an option as a decoppering agent in new systems due to recent environmental constraints placed upon the system/charge (Andrulis Research Corporation 1994). Ironically, artillery soldiers' baseline blood lead levels are lower than that of the general population (Smart et al. 1994).

Interestingly, coppering experiments recently performed by the Navy (Peters 1995) on two 5-in/54 guns show that firing charges without a decoppering agent in different guns result in different coppering behaviors. After more than 100 nondecoppering charges were fired, one of the guns did not copper at all, while the other gun coppered quite a bit. Thus, experiments with alternative decoppering additives will be inconclusive if copper does not appear on the bore surface. A copper-laden barrel must be fired with charges containing the alternative additive to verify their "decoppering" capability.

Selective electropolishing is proposed as an alternative or in addition to charge additives. Implemented as a part of regular maintenance, this process is relatively simple, using proven technology (U.S. Patents and Lafleur 1995) to remove copper from the bore. Selective electropolishing utilizes preferential oxidation and dissolution of the elemental material to be removed. To exploit this process, a current is passed through an electrolyte solution between a cathode and the barrel. Due to the physical configuration of the barrel, a rod was chosen as a cathode, electrically insulated from the barrel by a pair of sealing nylon bungs. A weak ammonium hydroxide solution was chosen as the electrolyte to reduce the possibility of iron corrosion, prevent the release of oxygen, and produce soluble copper oxides. The electrochemistry of the process is covered in the following section, with a discussion on the potential for bore surface damage.

2. DESCRIPTION OF ELECTROCHEMICAL DISSOLUTION OF COPPER FROM IRON-BASED SURFACES

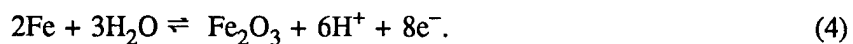
The electrochemical deposition and dissolution of metallic copper is relatively simple, and, in fact, has been used for over 70 years to produce high-purity copper. The fundamental reactions involved in this process are



where E° is the reversible potential vs. the standard hydrogen electrode (SHE) potential. The reactions in acid solutions are complicated by the thermodynamic tendency for copper (I) to disproportionate according to



The problem in electrochemically oxidizing metallic copper in acidic media (reactions [1] and [2]), in the presence of iron, is that significant corrosion of the iron will also occur. This is readily shown by reference to the Pourbaix diagrams in Figures 1 and 2, following (Cockett and Morgan 1958). As shown in Figure 1, attempts to oxidize an Fe electrode in acid solution will dissolve Fe as either Fe^{2+} or Fe^{3+} depending upon the anodic potential. In alkaline solution, and depending upon pH, a number of insoluble solid phases (various oxides and hydroxides) will form, but in highly alkaline solutions (pH ~14), again Fe can oxidize to the soluble species HFeO_2^- . At extremely high anodic potentials (not well defined in Pourbaix [1966], but above 1.6 V vs. the reversible H_2 electrode [RHE] discussed next), oxygen evolution will occur. In a moderately alkaline solution, Figure 2 shows that Fe will passivate by forming a stable film of Fe_2O_3 . In this process, Fe is oxidized according to



Once the passive film forms, no further reaction will occur other than oxygen evolution from the passive film surface. Because of the restricted pH range, and because the ammonium ion is helpful in the dissolution of copper, a 0.5-mol dm^{-3} NH_4OH aqueous solution (~2 mass %) of pH = 11.4 was chosen for our laboratory studies.

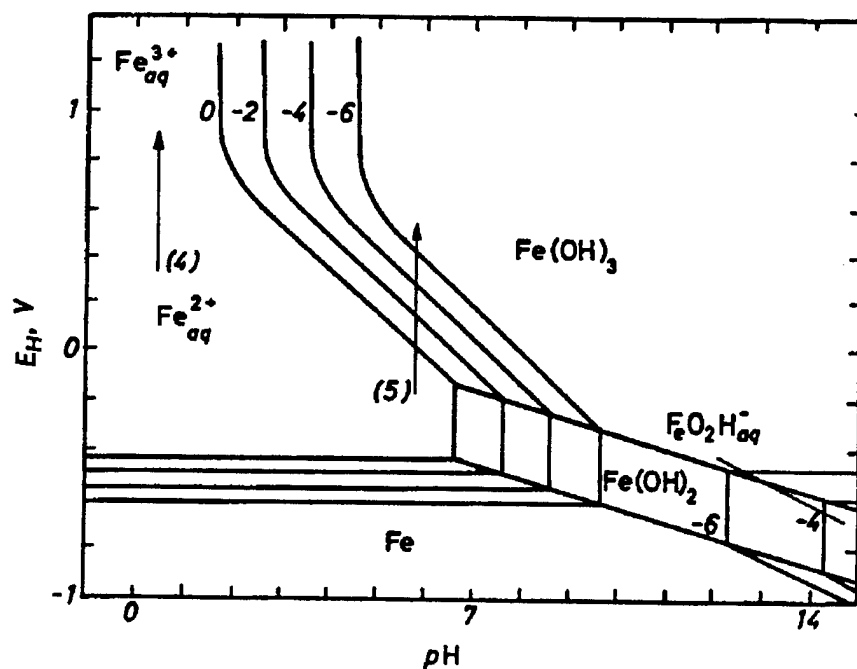


Figure 1. Pourbaix diagram for the Fe-H₂O system at 25° (only Fe, Fe(OH)₂, and Fe(OH)₃ solid phases are shown).

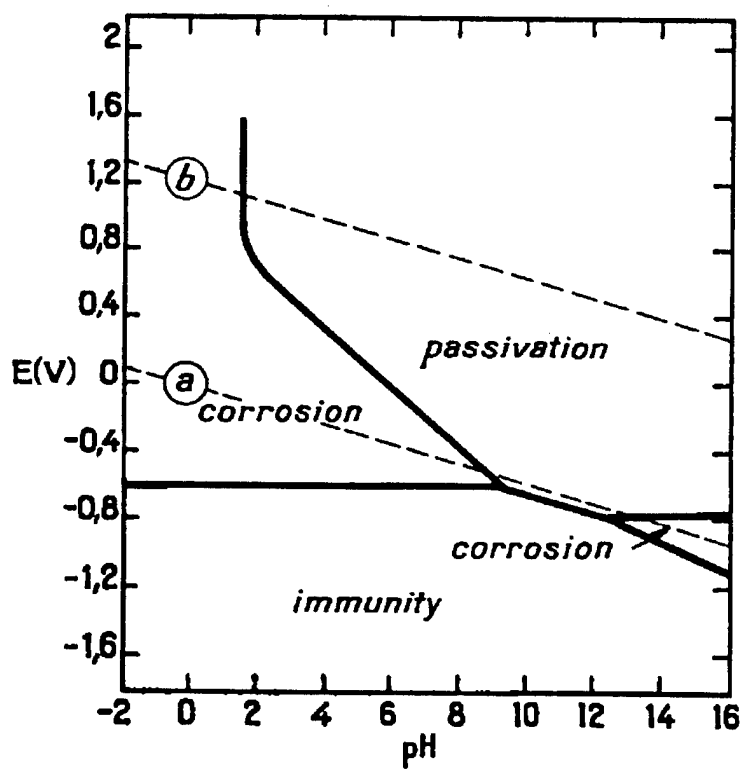


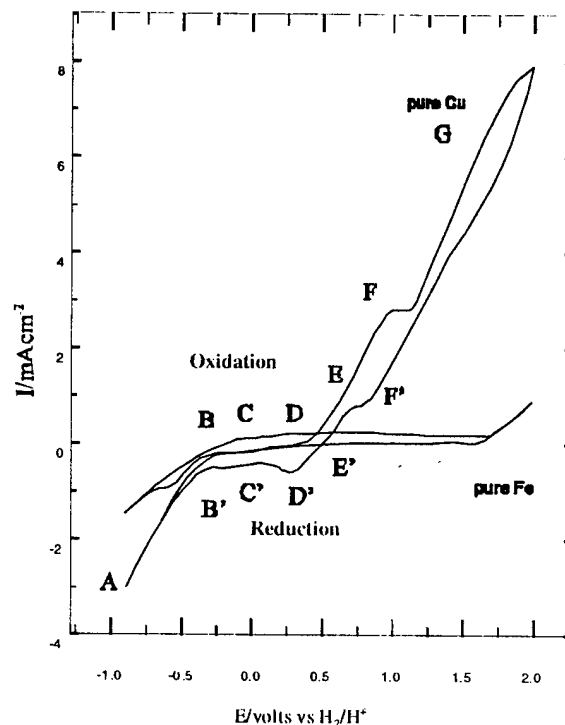
Figure 2. Calculated regions of corrosion, immunity, and passivation by a film of Fe₂O₃. O₂ evolution occurs above the dotted line b, and H₂ evolution occurs below the dotted line a.

Copper treated anodically in alkaline solution is known to passivate, first forming Cu_2O , which is further oxidized to cupric oxide (CuO). At high anodic potentials, in addition to oxygen evolution, soluble copper species form, e.g., Cu_2O^{2-} , but, depending upon both temperature and pH, the insulating thick layer of CuO formed results in high electronic resistance that is accompanied by a drop in current (Mantell 1960). To produce soluble copper species and at the same time limit the anodic potential to minimize the evolution of oxygen, a strong copper ligand, e.g., NH_3 , is quite effective. To test the removal of copper from Fe surfaces, a number of controlled potential and controlled current experiments were performed and are detailed, following.

3. ELECTROCHEMICAL EXPERIMENTS

Figure 3 shows the cyclic voltammogram of the second sweep at a high-purity copper surface (0.07 cm^2) in $0.50\text{-mol dm}^{-3} \text{ NH}_4\text{OH}$ solution (pH ~ 11.4). All scans in the following figures were carried out at a sweep rate of 50 mV/s . Although the voltammogram appears complex, at least seven electrochemical reactions could be identified ranging from hydrogen (A) to oxygen evolution (G), while not evolving H_2 . These observed oxidation steps (A through G) and subsequent reduction steps (G through A) by reduction route $\text{F}' \rightarrow \text{B}'$ are listed in Table 1, following. While the exact processes occurring in the area labeled G in the figure are not completely clear, it is believed that a combination of copper dissolution and oxygen evolution is occurring (O_2 bubbles at the Cu electrode are visible in this potential range). As seen by comparing Figure 3 and Table 1, in the aqueous ammonia solution used in this study, the oxidation products of copper are readily soluble, thereby indicating the feasibility of dissolving copper electrolytically. In fact, the intense blue color of the copper-ammonia complex, $\text{Cu}(\text{NH}_3)_4^{++}$, is observed in the ammonia solutions after anodization.

The cyclic voltammogram for a high-purity Fe surface (0.06 cm^2) is superimposed on Figure 3. Because of the small currents observed at the Fe electrode, a complete interpretation of all the reactions occurring at this electrode is not possible, but based on the information discussed in regard to Figures 1 and 2, it is clear that at cathodic potentials starting at around -0.6 V , hydrogen evolution starts. There is a small cathodic peak at around -0.5 V on the voltammogram, which is believed to be the reduction of an oxide to metallic Fe. On the anodic sweep starting at around -0.4 V , the Fe electrode is passivated presumably by Fe_2O_3 , as indicated by the small (close to zero) currents observed up until the potential of around 1.6 V is reached. At this higher anodic potential, oxygen evolution begins. In the pH range provided by the $0.50\text{-mol dm}^{-3} \text{ NH}_4\text{OH}$ solution, we see no evidence of the formation of soluble Fe species.



Note: Region A does represent hydrogen deposition!

Figure 3. Cyclic voltammograms for iron and copper.

Table 1. Reactions Identified From the Cyclic Voltammogram of Pure Cu^a

Reaction	Electrochemical Oxidation Mechanism	E°
	$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$ (acid solution)	0.000
A	$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ (alkaline solution)	-0.828
B	$\text{Cu}(\text{NH}_3)^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{e}^- \rightleftharpoons \text{Cu}(\text{s}) + \text{NH}_4\text{OH}(\text{aq})$	-0.154
C	$\text{Cu}(\text{NH}_3)_2^+(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \text{e}^- \rightleftharpoons \text{Cu}(\text{s}) + 2\text{NH}_4\text{OH}(\text{aq})$	0.125
D	$\text{Cu}(\text{NH}_3)_4^{++}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s}) + 4\text{NH}_4\text{OH}(\text{aq})$	0.333
E	$\text{Cu}(\text{NH}_3)_4^{++}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \text{e}^- \rightleftharpoons \text{Cu}(\text{NH}_3)_2^{++}(\text{aq}) + 2\text{NH}_4\text{OH}(\text{aq})$	0.541
F	$\text{Cu}(\text{NH}_3)_4^{++}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) + \text{e}^- \rightleftharpoons \text{Cu}(\text{NH}_3)^+(\text{aq}) + 3\text{NH}_4\text{OH}(\text{aq})$	0.820
G	$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$ (acid solution)	1.229
	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-(\text{aq})$ (alkaline solution)	0.401

^a E° is the half-cell potential vs. the SHE.

The aforementioned experimental studies confirm that copper can easily be dissolved anodically, but that a passive oxide film will form over the potential ranges of interest. At high anodic potentials (see Figure 1), dissolution of Fe is possible, i.e., if the potential greatly exceeds 2 V. Upon the return (cathodic) scan, the passive film is reduced at around -0.5 V, shortly before hydrogen evolution occurs (see Figure 3). However, it is reasonable to assume that hydrogen embrittlement will occur when hydrogen is evolved from iron, or particularly from a hardened steel gun tube.

To further investigate these findings, dissolution of copper under constant current conditions was investigated, particularly to determine the effect of rate upon dissolution and corrosion of iron. A Teflon-shielded, polished iron rod with an exposed surface area of 0.196 cm^2 was electrochemically plated with 0.025 mm of copper from a saturated $\text{Cu}(\text{NO}_3)_2$ solution at 100 mA for 60 s. The copper-plated rod was placed in the cell containing a $0.50\text{-mol dm}^{-3} \text{ NH}_4\text{OH}$ solution and was then anodically cleaned at 25 and 50 mA cm^{-2} , using a stainless steel counter electrode. Anodic cleaning at 50 mA cm^{-2} for 25 min resulted in complete dissolution of copper from the Fe substrate, but visible pitting and oxidation were evident on the surface of the iron. Anodic cleaning at the smaller current density of 25 mA cm^{-2} for 35 min produced a copper-free surface with no visible corrosion of the iron substrate. The blue color of the complex $\text{Cu}(\text{NH}_3)_4^{++}$ was clearly visible at the end of this process. The rate of removal of copper at this lower rate was found to $7.5 \cdot 10^{-4} \text{ mm/min}$, or about 1 mil/min. We conclude that the electrochemical dissolution of copper from an iron surface can be safely accomplished at the lower anodic rate of 25 mA cm^{-2} .

4. ANALYTICAL POTENTIAL FIELD INVESTIGATION

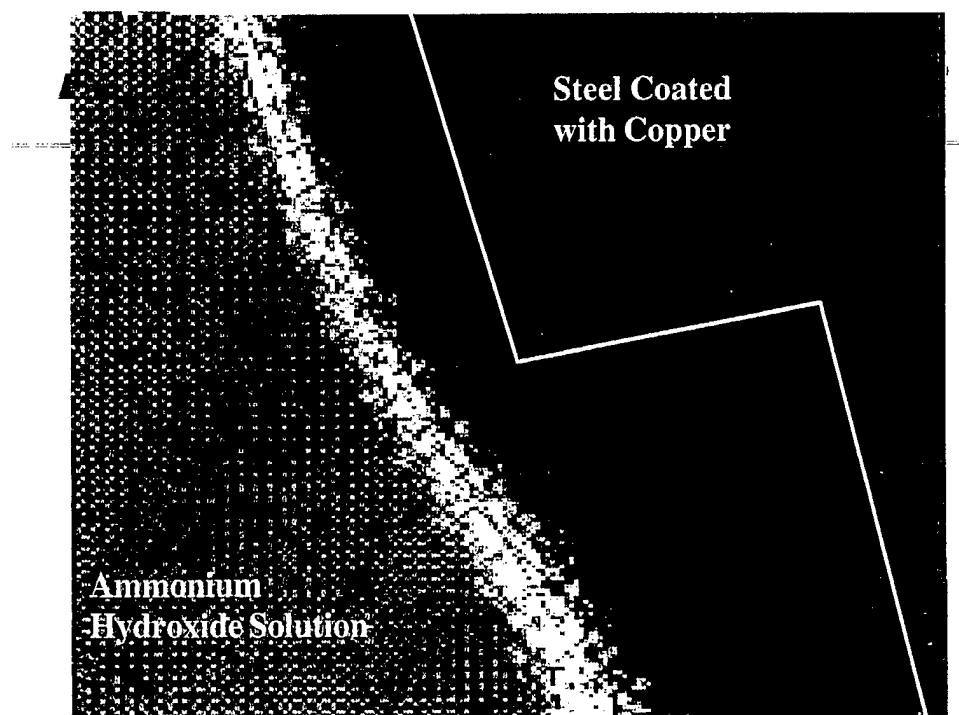
Because only two coppered VIC regenerative liquid propellant gun (RLPG) tubes were available for the experimental demonstration portion study, numerical calculations were performed to describe the influence of the lands and grooves on the applied potential field between the gun and electrode. It was thought that there might exist some concentration factor near the corners of the lands that would result in a region of local high potential which may electropolish (round) the corners. These calculations were made using Algor, a finite element package containing electrostatic computational capabilities. The parameters in the calculations included electrodes of different diameter and differing electrolytic conductivity, as well as the applied potential level. The potential was applied between the cylindrical cathode and the outside of the barrel, allowing the potential field to generate itself rather than applying the potential to the land/groove surface of the barrel.

Figure 4 shows the potential field around the bore surface in a region including a land groove junction for a cathode 1.9 cm diameter (0.75 in) with a conductivity of household ammonia (1.0 mmho/cm). The voltage scale in the figure is from 0.70 to 0.75 V. This very fine scale is required to reveal the variations in the potential field. Hence, the radial variations in the field are fairly small for a 0.55-cm electrode, and the resulting concentration factor produced by the corner does not pose a problem for the operation. The calculations provide some insight into what occurs during the process. As can be seen in Figure 5, the current flux levels are very nonuniformly distributed over the lands and grooves. This calculation was performed assuming a uniform copper deposit over the surface, again with the imposed potential applied to the outside of the barrel. What this current flux plot shows is that the copper (current) will initially flow from the outside edges of the lands. As the copper is removed, the current location will move to the center of the land. Once the land is clean, the middle of the groove will be the next location for copper removal. The copper removal finally ends with the corners of the groove. Operationally, this description is fairly important, as the last stage of copper removal will be in the grooves. The maintenance of the groove definition will require that attention be paid to continuing the application of the potential until enough copper is removed.

5. METALLURGICAL ASPECTS OF DECOPPERING

5.1 Decoppering Agent History. Coppering of gun tubes was a serious problem by 1916. In August 1917, the French had discovered that if the base plates of shells were coated with solder (lead-tin alloy), the deposits of copper in the bore "were soon converted to a brittle tin bronze and blown out of the gun" (Cockett and Morgan 1958). By March 1918, the French had proposed the use of foil containing 60% tin and 40% lead to be placed on the top of the propellant charge. Since that time, lead in the propelling charge has been used to decopper large-caliber weapons. It is used as the metal foil in Army artillery systems (1.3% of charge weight in the M203E1), and as the carbonate in Naval gun systems (1.0% in NACO).

5.2 Mechanism of Coppering. To understand decoppering, we must first understand coppering. Both mechanisms can (and usually do) occur simultaneously. "Coppering" means the progressive transfer of copper (or copper alloy) from the projectile's rotating band to the bore of the gun tube. As established by Montgomery (1976), projectiles are melt-lubricated during nearly their entire travel down the gun tube. The lubricating liquid metal film (LMF) forms just after the rotating band is fully engraved, in the first inch or two of travel. Some of the copper in the LMF that the projectile rides on is transferred to the gun tube bore.



Finite element electrostatic calculation at the bore surface, scale is 0.70-0.75V

Figure 4. Finite element calculation of potential field. (Scale is 0.70 to 0.75 V).

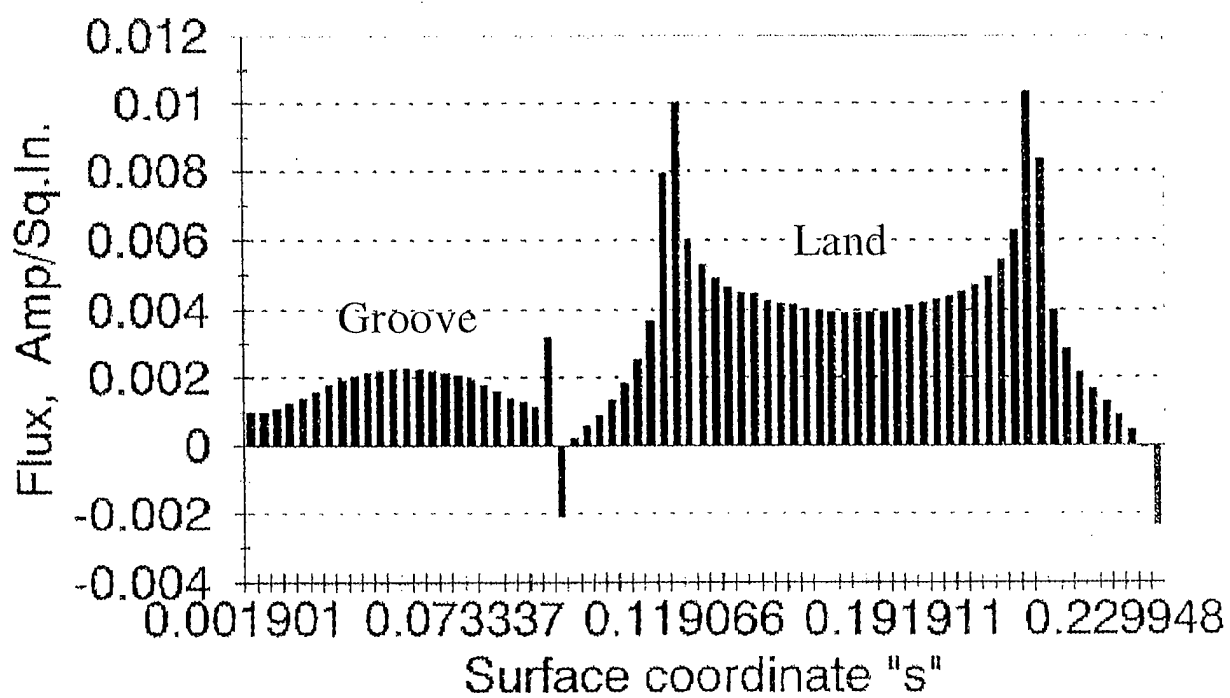


Figure 5. Steady-state surface current flux.

As the charge is increased, the amount of driving edge wear of the rotating band is increased, and the amount of coppering is increased. Wear of the driving edge is primarily due to the allowable bearing stress of the LMF-rotating band combination being exceeded. It is important to note that the LMF exists primarily due to frictional heating rather than propellant gas or gun tube heating, and that copper is transferred in the liquid phase from the rotating band to the gun tube bore via the LMF. This is supported by work by Montgomery (to be published) on recovered 155-mm RLPG projectiles. Examination of the projectile boat tail showed a pattern of solidified small copper droplets emanating from the driving edge of the rotating band.

As the driving edge wear of the rotating band increases as the projectile travels down-bore, the rotating band land becomes thinner. At some point the remaining band land cannot support the applied shear stress, and the lands shear off. This is termed "band stripping." Band stripping can occur earlier in shot travel if the projectile is subjected to a high torsional impulse from either rifling or charge anomalies. Copper from this source is in the form of loose, solid chunks and thus should not contribute significantly to coppering.

5.3 Mechanisms of Decoppering. As noted previously, the first speculation on the mechanism of decoppering was that the deposits of copper in the bore "were soon converted to a brittle tin bronze and blown out of the gun." In the Dictionary of Explosives and Related Items of 1966 (Federoff and Sheffield), this mechanism was also advanced.

In 1975, Robertson examined the lead-copper phase diagram, and concluded that this mechanism was very unlikely since there are no lead-copper intermetallic compounds and "since lead does not alloy with copper to any measurable extent unless the copper is also melted." (However, as noted previously, copper is deposited in the liquid phase.) Robertson proposed an alternative mechanism: that lead removes copper in gun barrels by melting and depositing on the coppered bore as a liquid or dissolving the copper, and that the liquid lead with copper in solution is carried out of the tube still in the liquid phase.

Based on high-pressure, high-temperature investigations, Vezzoli and Otooni later proposed that liquid lead diffuses through the copper film at gun tube pressures and embrittles the copper, causing it to break up under the action of succeeding projectiles and gas wash. This phenomenon is known to metallurgists as liquid metal embrittlement, and occurs with a number of combinations of metals. Basically, a liquid metal that wets the surface of a substrate metal will also tend to wet the grain boundaries. The liquid

metal travels into the substrate via the grain boundaries, thereby weakening it. The substrate will then tend to fracture along the coated boundaries. In support of this mechanism of de-coppering, lead and tin inclusions in brass are known to cause severe embrittlement when tested near the melting point of these inclusions (American Society of Metals [ASM] 1986).

A fourth possible mechanism can be proposed. When a string of leaded charges are fired, the deposit on the gun tube may be: Cu-Pb-Cu-Pb-Cu-Pb-... This is a very weak structure (similar to graphite), especially when heated, and the layers are sloughed off with each passage of a projectile. The number of layers formed is indeterminate if this is the operating mechanism.

5.4 Deleterious Effects of Decoppering Additives. Not only do lead decoppering additives comprise a large parasitic charge mass, they can also cause premature gun tube failure. Independent from the possible liquid metal embrittlement of the copper film by lead, it has been shown that lead, in the liquid phase, also embrittles steels by liquid metal embrittlement (Cockett and Morgan 1958). Furthermore, because the gun tube is thermally cycled through the melting point of lead, lead is forced into cracks in the gun tube in the liquid phase and solidifies, wedging the cracks open. As the gun tube continues to be cycled, these cracks are ratcheted open.

5.5 Long-Term Solutions to the Problem. Each of the reports by Robertson (1975) and Vezzoli and Otooni indicate that bismuth should be as good or better a decoppering agent than lead. They indicate that it has melting and boiling points somewhat lower than lead, and a very similar phase diagram with copper. Copper is more soluble in liquid bismuth than liquid lead, and bismuth wets copper much better than does lead, leading to greater liquid metal embrittlement. The embrittlement effect of bismuth for copper and its alloys is well documented, while liquid bismuth does not appear to embrittle steel (American Society of Metals [ASM] 1986). Because bismuth also has a very low toxicity, it would appear to be an ideal replacement for lead as a decoppering agent. Studies by the U.S. Army and the U.S. Navy are currently underway to verify its effect.

Another long-term solution to the coppering problem is to use copper-free rotating bands on new projectiles. Soft iron (commercially pure iron, weld-overlay) bands will produce no coppering. Soft iron can be used because the as-deposited hardness is about the same as copper, but both the melting point and the allowable bearing stress are quite a bit higher, giving much less wear. Excessive band wear has been

seen in projectiles fired at top zone from developmental 52+ caliber 155-mm cannons. Projectiles **may require** soft iron bands to prevent band stripping when fired at muzzle velocities approaching 1,000 m/s.

Furthermore, it is possible that any iron that deposits may be beneficial: it may act to "heal" preexisting cracks in the chromium plating, preventing attack of the underlying gun steel by propellant gasses. However, the slow-speed sliding properties of soft iron on chromium-plated steel may not be as good as copper alloys, and an iron band must be coated to prevent rust. Large-caliber soft iron rotating bands are being studied by the U.S. Army.

6. SELECTIVE ELECTROPOLISHING EXPERIMENT

Two copper-fouled 30-mm U.S. Army Research Laboratory (ARL) RLPG barrels were donated for this study. Liquid propellant guns are a good source of coppered gun tubes as the liquid propellant does not lend itself to the addition of decoppering agents due to compatibility issues. The barrels were set vertically so as to mitigate the bowing of the cathode, as well as to facilitate drainage of the electrolyte. A vacuum fluid fill system was constructed to facilitate the filling and flushing of the barrels. Household ammonium hydroxide (ACME brand) was used as the electrolyte (about 2% molar concentration) due to its alkaline nature and because it is a strong ligand for oxygen that prevents the evolution of oxygen. A regulated DC power supply with a current range up to 6 A was used to provide the potential. The desired data from the experiment included the current through the power lines and the voltage across the line. An inductive current meter was clipped over one of the four 10-gauge power lines. This device provided a voltage output proportional to the current that was recorded on a Nicolet 4094 digital oscilloscope and Cole-Palmer strip chart recorder. The potential was also recorded on both the Nicolet and strip chart recorder. The experimental setup is schematically presented in Figure 6.

Figures 7 and 8 contain the first and second medium-caliber (30-mm) selective electropolishing (decoppering) voltage and current data. The experiments were performed using a constant voltage power supply set to 0.75 V, as can be seen in the figures. It was noticed during the experiment that an initial potential of 87 mV existed with the ammonia present before the power supply was connected. The current, above the nominal value provided by the conductance through the ammonium hydroxide solution, is proportional to the surface area of the copper. The current decay represents regions of copper being removed from the surface as well as the free ions associating themselves with the electrodes. The sharp

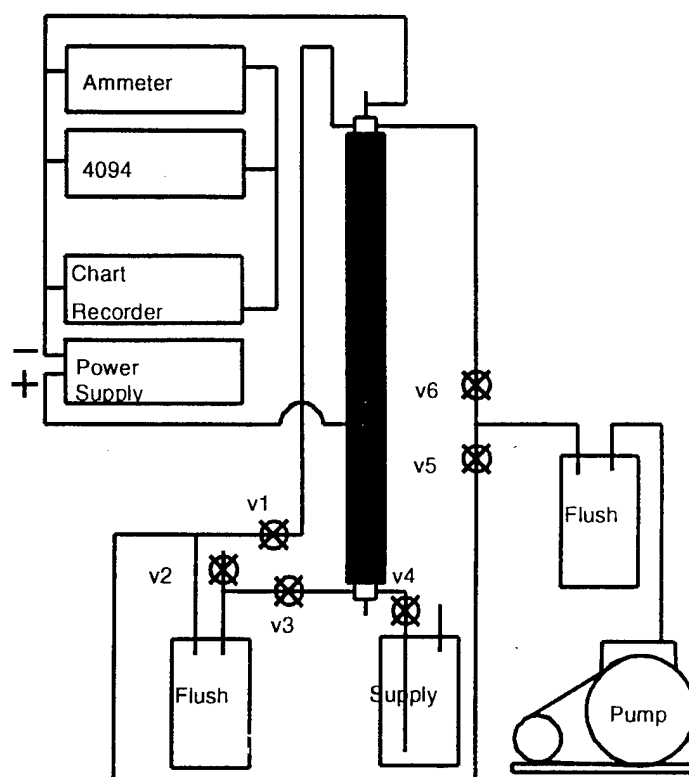


Figure 6. Electropolishing experimental setup.

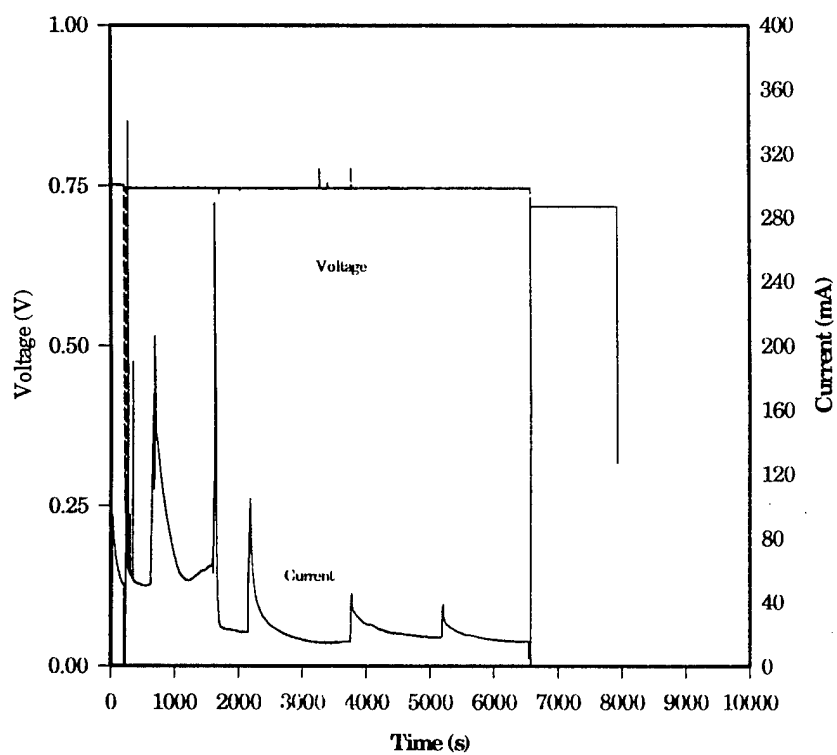


Figure 7. Current and voltage data from the first 30-mm electropolishing experiment (barrel A).

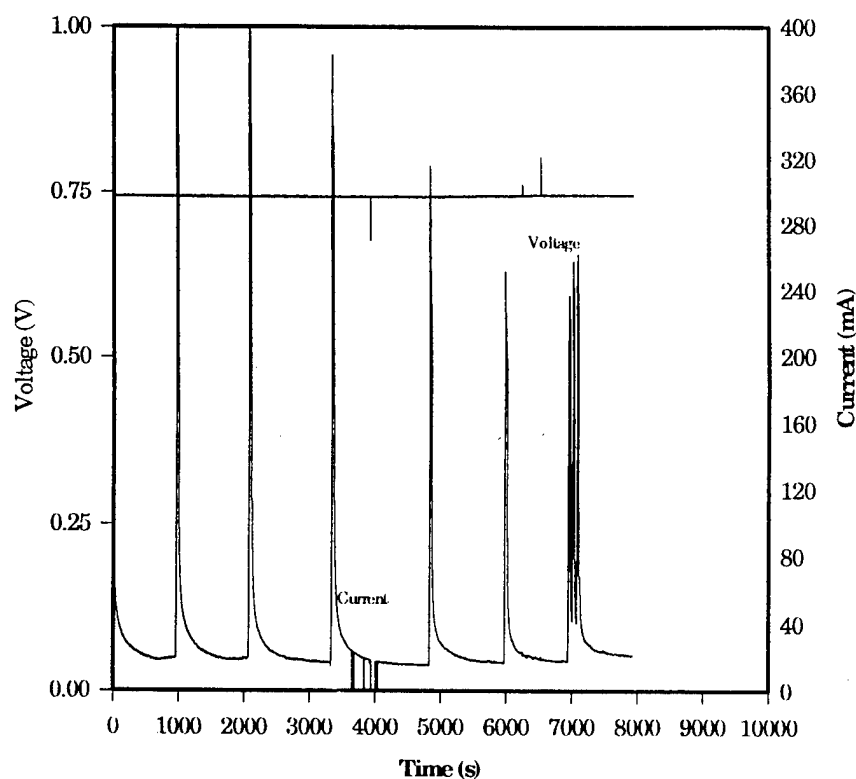


Figure 8. Current and voltage data from the second 30-mm electropolishing experiment (barrel B).

current peaks in Figure 7 are from when 500 ml of fresh ammonia were drawn into the barrel from the bottom. This "flushing" was performed because of what appeared to be a premature steady-state current. On the expanded time scale of the strip recorder, steady state is readily recognized. Typically this process requires about 20 min for small arms (Lafleur 1995 and Brant 1995). After the second flushing, the decay was somewhat abnormally affected (abnormal is relative, as this effect has not been seen before). The subsequent rise in current, during the third current decay period, is believed due to the flocculent nature of the blue copper precipitate, which was most likely shorting out the electrodes. The vacuum lines on the third flush were clogged with this precipitate and perhaps other solids. The barrel was initially swabbed, but was evidently still very fouled with residue as the blue solution was a muddy, brownish blue color for the first three flushes. As the experiment proceeded, each subsequent flask of withdrawn fluid had a fainter and fainter blue tint. The peak current decreased with each flush, as seen in Figure 7, perhaps reflecting the decreased surface area of copper. After four flushes, the current continued to asymptotically decrease to about 15 mA, despite repeated further flushes. It was deemed at the end of the seventh decay that all copper was most likely removed, and the experiment was ended.

The current and voltage for the second barrel are presented in Figure 8. This barrel contained much less fouling material than the first barrel. The withdrawn fluid was initially much cleaner from this barrel and was a brilliant blue, due to the presence of $\text{Cu}(\text{NH}_3)_4$. Following successive electropolishings, this brilliant blue color gradually faded in the withdrawn fluid until it was almost clear. It is interesting that the current peaks during the flushes for this barrel are much higher than those from the first barrel. This may be because this barrel was cleaner and perhaps did not have as much iron oxide on the bore surface, thus allowing easier passivation. This experiment was continued even though a steady-state current of about 15 mA was reached very early. We desired to see if the current spikes during flushes would decrease as in the first barrel. Indeed, as seen in Figure 8, the magnitude does decrease, but not so drastically as in the first barrel. Near the end of this experiment, repetitive flushing was performed to represent a continuous flush system that would recirculate the electrolyte through a filter and the barrel by means of a pump. The peak current increased with each flush of the repetitive series.

Figures 9 and 10 contain the star-gauge data for both barrels used in the selective electropolishing decoppering experiment. The solid lines are the bore deviation data taken before the experiment, while the dotted lines show the star-gauge data after the experiment. It is apparent that indeed some material was removed from both barrels. Typically this was on the order of 1/1,000 of an inch. (The precision of the stargage equipment is 1/1,000 of an inch.) When initially bore-scoped it was noticed that barrel A contained a lot of rust, whereas barrel B did not contain so much rust. Barrel A was indeed exposed to an oxidizing environment for quite some time before the experiment. One reason so much material was removed from barrel A is that the duration of the experiment was longer, and that the oxide layer was brushed before stargaging. Furthermore, these barrels were extremely coppered, having hundreds of brass projectiles fired through them without any attempts to remove the copper. The macroscopic copper (streaks) visible in the bore-scope video tape before the experiment were not present in the bore-scope tape after the experiment. However, there appeared in the grooves of both barrels after the experiment a very fine uniform copper finish which was not present before. This is possibly due to the amount of copper originally in the grooves and the fact that the experiment was not performed long enough, or that copper from the $\text{Cu}(\text{NH}_3)_4^{++}$ replated the surface after the experiment. More investigation into the reasons for this resultant finish are required in future studies.

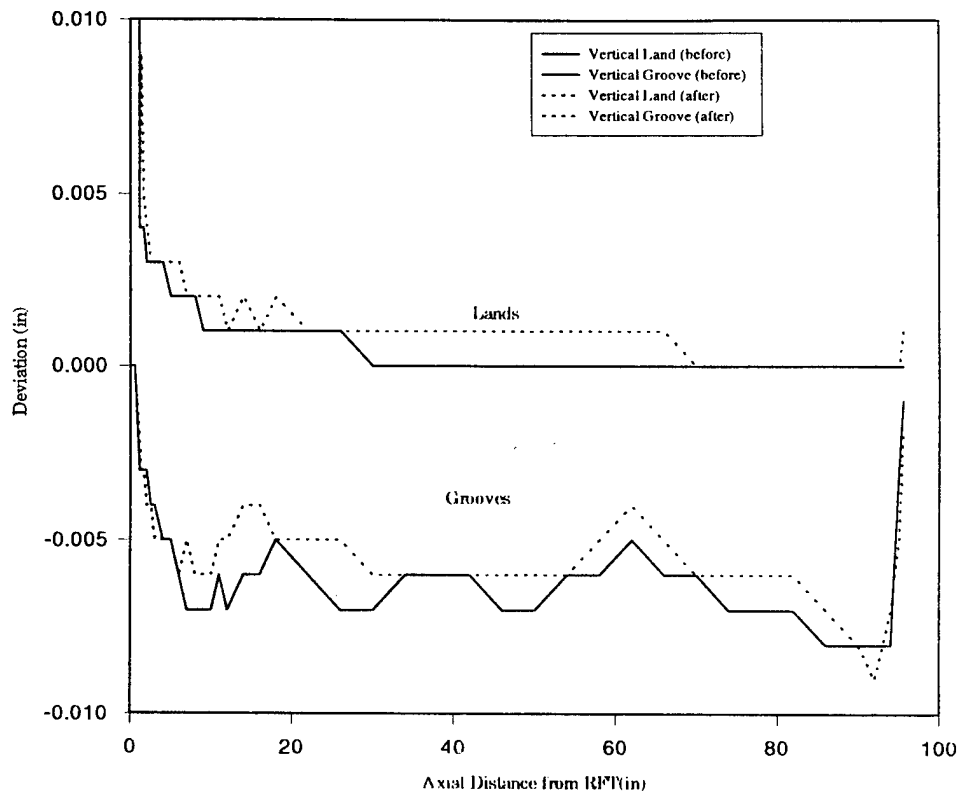


Figure 9. Stargage data for barrel A.

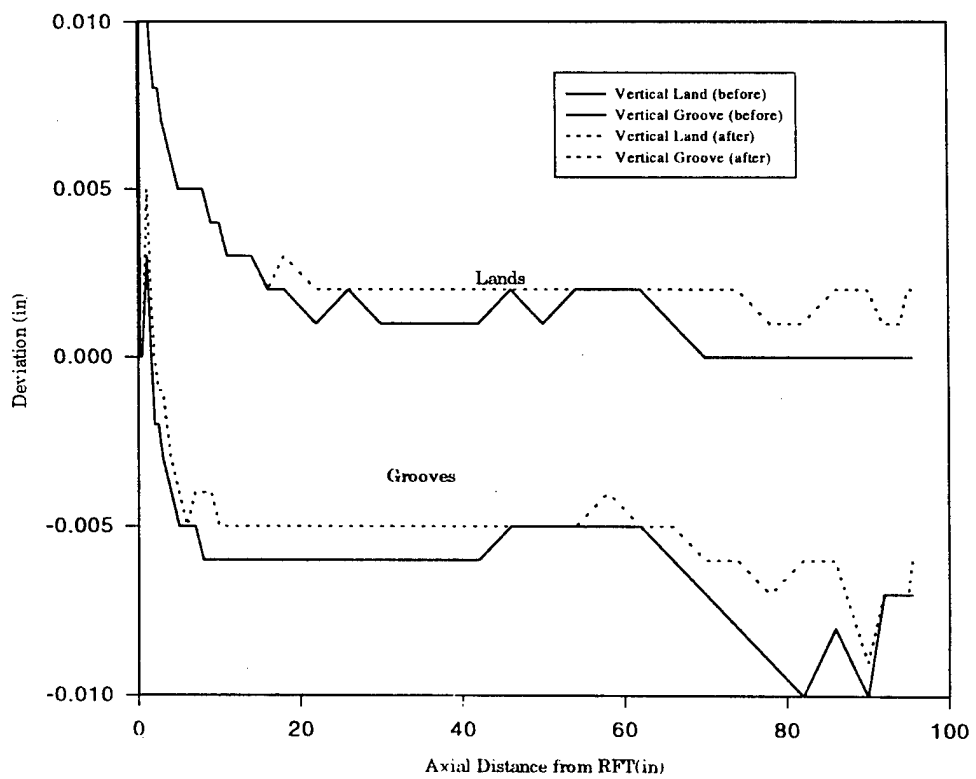


Figure 10. Stargage data for barrel B.

7. DISCUSSION

We have successfully demonstrated an alternative decoppering technique in which all macroscopic copper deposits are removed from both barrels. Electrostatic calculations have shown that the copper will be removed from the lands first and the inside corners of the grooves last. An ammonium hydroxide solution appears to perform as well as the electrolyte due to its behavior as a strong copper ligand, its passivation of iron, and its minimization of oxygen evolution.

Some of the issues to be addressed in the future involve the amount of material removed, as well as determining when decoppering is completed. The extracted solution's blue intensity gave some indication of the progress. Flocculents shorted the electrodes and blocked the extraction lines during the experiment. Further research into aprotic electrolytes will likely indicate a candidate electrolyte that will not cause passivation, thereby reducing the amount of bore material removed. Small laboratory-scale experiments are required to determine the characterization of the process. The presence of chromium in future artillery systems requires studies addressing the effects of the process upon a chromed surface. Chromium will most likely benefit the current technique as it will not oxidize and will behave inertly as long as the applied potential remains below the chromium oxidation potential. These small-scale experiments will assist in evaluating and guiding the gun-scale experiments. Experimental studies and post-firing analysis are desired to evidence the metallurgical hypothesis proposed concerning the mechanism of Pb and Bi alloy decoppering. This work would be connected with the large-caliber test firings by designing and analyzing test probes inserted into the gun.

Other future work will involve constructing and implementing a 155-mm fieldable system. This system would utilize a filtered, closed recirculation loop for the electrolyte. The design must account for implementation as part of a regular maintenance schedule. Interestingly, different guns most likely will have differing coppering rates, while some may not copper at all (NOSIH 1995). It is possible that the muzzle velocity radar system on the weapon may be able to dynamically indicate how much copper has built up.

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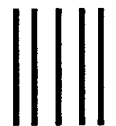
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