

The Structure, Redox Corrosion and Protection of Commercial Lead-Antimony Shot.

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ABSTRACT: Scanning electron microscopy (SEM) reveals commercial lead shot to be dendritic in nature and contaminated by substantive amounts of lead oxide and sulphate. Measurements of the comparative corrosion of lead shot in acid rainwater show commercial lead-1.25% antimony alloy corrodes 22 times faster than pure lead. This corrosion can be significantly accelerated by iron oxides produced by co-corrosion of commercial steel shot. Comparable studies of 'post fired' Integrated Fixation System (IFS) protected lead-antimony shot showed significant stability to acid rainwater. Microscopy shows corrosion is impeded by formation of a lead sulphide scale. Corrosion rates indicate that given a surfeit of acid rain, pure lead shot might last 21,000 years, commercial lead-antimony shot would survive only 1,200 years and in the presence of high amounts of iron oxides this would reduce to 190 years. By contrast, the corrosion rate of the Integrated Fixation System protected shot implied a corrosion time of approximately 1.5 million years. Results from this study indicate that in addition to accelerating lead corrosion, the firing of steel shot on ranges already containing lead shot will adversely influence site pH and provide a 'transport metal' which will facilitate migration of lead, antimony and other heavy metals from the contaminated site. Furthermore, commercial steel shot corrosion gave rise to manganese and nickel corrosion products as additional undesired pollutants.

INTRODUCTION:

Lead is still the material of choice for use in ammunition despite concerns over its environmental impact. Its density, malleability and ready availability gives lead significant ballistic, production and cost advantages over substitute materials. Worldwide, the market for ammunition projectiles equates to some 250,000 to 300,000 tonnes of lead alloy annually. Of the worldwide market, approximately 70% of lead is fired over confined ranges e.g. for trap and skeet shooting, significantly contaminating small parcels of land.

Concern about lead poisoning of wildfowl in wetland areas has given rise to restriction of lead in that application. As a consequence, a number of alternative materials have been promulgated as lead substitutes. These materials include; soft iron/steel, bismuth, tin, copper, heavy steel or Tungsten/Nickel/Iron steel (TNI) and Tungsten/Nylon-12 composites. Steel shot is comparable in cost to lead shot but lacking lead's density it requires a larger calibre shot to achieve comparable ballistic performance. It is also comparatively harder. Nevertheless, whilst not a perfect substitute for lead, for the price sensitive range shooting market, steel is presently the closest if not the only commercially viable alternative for civilian use.

With growing concern over range contamination there is increasing pressure from environmentalists, regulators and some shooting industry ‘experts’ to utilise these alternative materials for range shooting applications. Whilst well meaning in intent, many of these recommendations have been made in ignorance of the environmental implications arising from the chemistry of the materials in question and ill informed judgements as to the purportedly ‘non-toxic’ and ‘inert’ nature of the proposed alternatives.

Redox reactions are of particular importance in the chemistry of metals. They are electrochemical reactions where one metal will sacrifice itself and corrode in the presence of the more ‘noble’ metal, e.g. zinc corrodes to protect iron from rusting. This is the so-called ‘galvanic effect’. The relative reactivity of metals is given by the a list of chemical redox reactions and their associated voltages known as the Electrochemical Series and this is a useful and commonly used tool for predicting likely adverse metal interactions.

Certain projectile alloys based on tungsten have been shown to corrode rapidly via redox reactions, increasing potential hazard from projectile residues^(1,2). The low risk assessment of pollution from these materials has been entirely dependent upon the optimistic assumption that strong sorption to soil based minerals will retain their corrosion products permanently, and that site saturation and/or facilitated transport of these corrosion products will not cause contamination to migrate⁽³⁾, contrary to what is observed in the case of lead and other heavy metals⁽⁴⁾.

TABLE 1
Electrochemical Series of Selected Ammunition Metals

Equation No.	Redox Reaction	Redox Potential E⁰(volts)
1	$\text{Bi}^{3+}_{(\text{aq})} + 3\text{e}^- \rightarrow \text{Bi}_{(\text{s})}$	+ 0.381
2	$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Cu}_{(\text{s})}$	+0.3419
3	$\text{Sb}^{3+}_{(\text{aq})} + 3\text{e}^- \rightarrow \text{Sb}_{(\text{s})}$	+0.11
4	$\text{W}^{3+}_{(\text{aq})} + 3\text{e}^- \rightarrow \text{W}_{(\text{s})}$	+0.1
5	$\text{Pb}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Pb}_{(\text{s})}$	-0.1262
6	$\text{Sn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Sn}_{(\text{s})}$	-0.1375
7	$\text{Fe}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Fe}_{(\text{s})}$	-0.44
8	$\text{Ni}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Ni}_{(\text{s})}$	-0.4257
9	$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Zn}_{(\text{s})}$	-0.7618
10	$\text{Mn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Mn}_{(\text{s})}$	-1.185

The electrochemical series of selected ammunition materials **TABLE 1** would predict that addition of bismuth, copper or tungsten to metallic lead contaminated soil will accelerate corrosion of the lead, whereas the presence of lead and antimony will accelerate the corrosion of tin. Most significantly it predicts that antimony will corrode lead. Also a prediction that should cause concern would be that tungsten could liberate ionic nickel from TNI. This might not be significant with broad distribution in the environment under condition of a weak electrolyte such as acid rain⁽⁵⁾ but with concentration on a range in the presence of stronger electrolytes as can occur in soils or biological systems this might prove significant.

By following on the Redox analogy above, iron being a less noble metal than lead might reasonably be anticipated to precipitate soluble toxic lead salts in contaminated soils. The implication being that shooting steel shot onto lead contaminated land would remediate it. To this effect, iron shot and iron filings have been employed as heavy metals remediation agents. In the treatment of lead contaminated land there have been reports of an initial beneficial effect. However, it has been noted that subsequently the leaching of soluble lead salts occurs worse than before⁽⁶⁾. This added complication is due to the fact that the compounds of metals also exhibit their own redox potentials and those of iron oxides are particularly important in materials science, (see **TABLE 2**). Other phenomena that effect the redox corrosion of alloys are the grain size of the microcrystalline structure and the presence of impurities which can act as corrosion accelerating electrolytes.

TABLE 2
Electrochemical Series of Iron Oxide Reactions

Equation No.	Redox Reaction	Redox Potential E ⁰ (volts)
11	$\text{FeO}_4^{2-} + 8 \text{H}^+ + 3 \text{e}^- \rightarrow \text{Fe}^{3+} + 4 \text{H}_2\text{O}$	+2.2
12	$\text{HFeO}_4^- + 2 \text{H}^+ + 3 \text{e}^- \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$	+2.09
13	$\text{HFeO}_4^- + 4 \text{H}^+ + 3 \text{e}^- \rightarrow \text{FeOOH} + 2 \text{H}_2\text{O}$	+2.08
14	$\text{HFeO}_4^- + 8 \text{H}^+ + 3 \text{e}^- \rightarrow \text{Fe}^{3+} + 4 \text{H}_2\text{O}$	+2.07
15	$\text{Fe}^{3+}_{(\text{aq})} + \text{e}^- \rightarrow \text{Fe}^{2+}_{(\text{aq})}$	+0.771
16	$2\text{Fe}^{2+}_{(\text{aq})} + 1/2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+}_{(\text{aq})} + 2 \text{H}_2\text{O}$	+0.46
17	$\text{Fe}_2\text{O}_3 + 4 \text{H}^+ + 2 \text{e}^- \rightarrow 2\text{FeOH}^+ + \text{H}_2\text{O}$	+0.16
18	$\text{Fe}^{3+}_{(\text{aq})} + 3\text{e}^- \rightarrow \text{Fe}_{(\text{s})}$	-0.37

Alternative Approaches to Changing Materials.

There have been a number of different methods investigated for the remediation of lead contaminated shooting ranges, from simple mechanical recovery to soil washing using acids to dissolve heavy metals and their salts. Soil washing with water is commonly used in mainland Europe at a cost of €40-65 per treated tonne. US costs are comparable at \$70-80 per tonne. Acid washing is naturally more efficient as it dissolves the lead metal fragments for complete removal but at over \$330 per tonne it is significantly more expensive. The aforementioned washing costs exclude any chemical treatment of metals residues to reduce toxicity. Such treatment of all hazardous residues prior to segregated landfill will soon be mandatory within Europe under the Landfill Directive 1999/EU/31.

A number of reagents have been evaluated for low cost in-situ remediation of contaminated soils. Molecular Bonding Systems™ (MBS) of Solucorp Industries Limited⁽³⁾, is probably the most technically effective of these reagents by its ability to reduce a broad spectrum of heavy metals below regulatory limits, its reduction of soil toxicity and its permanency of effect. This technology has been accredited by the US-Environmental Protection Agency (EPA) for the remediation of heavy metals contaminated sites and has been used for shooting range remediation^(7,8).

MBS is in reality a complex proprietary cement type material containing calcium sulphide. The risks of harm from toxic heavy metals wastes are dramatically increased if they are in soluble or latently soluble forms. MBS treatment converts soluble metal compounds into metal sulphides. The sulphide ores of heavy metals are stable and amongst the most insoluble of heavy metal compounds. They are of dramatically lower toxicity than other adducts.

The MBS approach has been extended to create Integrated Fixation System (IFS) technology. IFS utilize MBS by encasing it in a degradable matrix, such that it can be applied to manufactured products⁽⁹⁾. Application of a small quantity of a suitable IFS matrix to a bullet, or shot pellets would be sufficient to remediate the lead metal in the soil 'post firing'. The ability to remediate the polluting item mitigates the need to treat the whole site with consequential cost benefits.

The objectives of our work were to investigate the influences of redox reactions of ammunition materials used in the sport shooting market and evaluate the efficacy of IFS technology to prevent pollution through the inhibition or 'passivation' of the inherent materials chemistry of lead projectiles such that soil chemistry is not relied on to permanently retain potentially harmful corrosion products.

MATERIALS AND METHODS

Materials:

'Star' Brand No. 8 Lead shot (ex-Argentina); trace metals in mg/Kg: Cu, 8; Cr, <3; As, 55; Mn, 4 and Ni, 16. The antimony content uniformity was poor, nominally 2% but assayed at 1,250 mg/Kg +/-1,070 mg/Kg (90% confidence limit).

No. 6.5 steel shot, ex-Hull Cartridge. Trace metals in mg/Kg: Cu 79; Cr 150; As, 34; Mn, 3,400, (0.34%w/w); Ni, 130 and Sb, 1.9.

Pure lead shot (2 mm average diameter) >99.999%w/w purity, Sigma-Aldrich Limited

IFS shot was prepared by over-coating Star Brand lead-antimony shot with a 1% by weight dry coating of degradable IFS matrix containing MBS. The material used for leachate testing was test fired into ballistics gelatine and recovered.

Methodology:

We intended to investigate interactions of commercial lead shot with and without commercial steel shot in an acid rain environment so that we might discern the nature and relative magnitude of likely corrosion arising from their primary materials and their inherent contaminants and avoid possible complex interactions from clays and biomass sorption and soil based electrolytes which would obscure the primary corrosion processes.

There are 3 generally accepted procedures for leachate testing of soils; DIN 38,414(S4), US-TCLP and UK-NRA method. All these procedures are similar utilising CO₂ acidified water (at pH 6-6.5) as extraction media and a 1:10 sample to leachate ratio but they have some noticeable variations in extraction time, agitation and filtration methodology.

For the testing of high moisture samples, the DIN, TCLP and NRA procedures are deemed equivalent. Therefore by immersing our shot samples in water with only mild periodic agitation for periods of several days to months, we are able to take the supernatant liquor as a realistic model of what the corroding shot might liberate and this supernatant liquor sample would fulfil the technical requirements as an acceptable sample under all the aforementioned testing methods.

Leachate extracts from lead shot were prepared as follows: A number of individual samples by taking 10 parts by weight (pbw) shot and added it to 100 pbw of CO₂ acidified distilled water at pH 6.3 in a 500ml capacity sealable HDPE food grade plastic bottle. The samples were left to stand for a number of days at room temperature (circa 16-18°C), being periodically (approximately every 7 days) mildly agitated and visually inspected. Periodically a sample was harvested, the supernatant liquor decanted off the shot and the liquor sent to the Laboratory for filtration and analysis for soluble lead and antimony by Gas Plasma Spectroscopy (GPS). The analytical results were reported in mg/Litre and plotted against the time the shot sample had been leaching in days.

For the measurement of interaction of lead shot with steel shot, we modified our procedure was as follows: A number of individual samples by taking 10 pbw Lead shot, 10 pbw steel shot, added to 100 pbw of CO₂ acidified distilled water at pH 6.3 in a 500ml capacity sealable HDPE food grade plastic bottle. The sample was left to stand for a

number of days, being periodically (approximately every 7 days) mildly agitated and visually inspected. Owing to the generation of a significant amount of suspended iron oxide residues, at the end of the test period the suspension was decanted off the shot and the sample sent to the test Laboratory for the following analysis: pH, total metals (pre-filtration) and for soluble metals post filtration. The extracts for total metals were prepared by aqua-regia digestion of a portion of the suspension followed by dilution in deionised water, with metals content being analysed by GPS.

Metals testing was carried out by Analytical and Environmental Service of Wallsend Tyne and Wear, a UKAS accredited facility. Measuring, weighing and all dilution errors were estimated at +/-3.0% maximum. The cited laboratory accuracies of Gas Plasma Spectroscopy are +/- 11% at 0.010mg/Litre for metals excluding Sb and As which were analysed using hydride generation and Gas Plasma Fluorescence Spectroscopy. Laboratory accuracy was cited at +/- 11% at 0.005 mg/Litre.

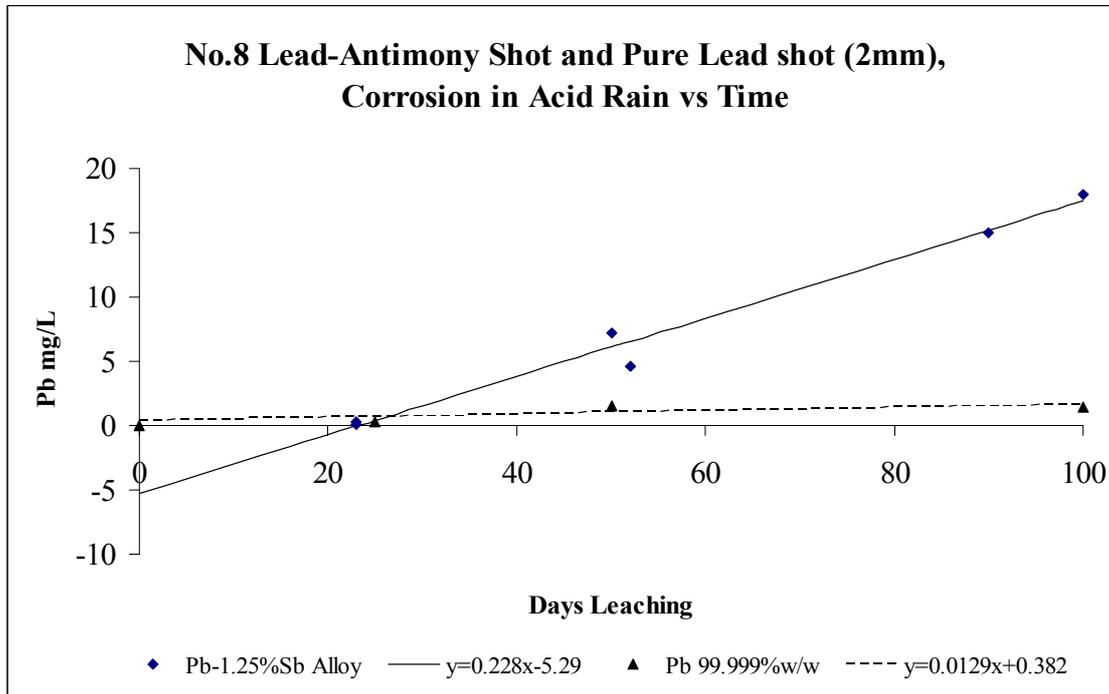
Determination of surface area was by inference of the mean diameter of the spherical shot particles and the known density of pure lead 11.3 g/cc and alloy shot under study of 11.0 g/cc.

Examination of test materials was carried out at the Department of Material Science, UMIST, Manchester. Samples of uncoated and IFS coated lead-antimony alloy shot were cold cast in resin. Cross-sectional slices were obtained, polished but left unetched to reveal the internal crystal structure of the shot. Uncoated cross sections illustrated as **FIGURES 6-8**. IFS coated shot cross-section, illustrated **FIGURE 9**. IFS coated shot following immersion in deionised water for 3 days, illustrated **FIGURES 10-12**.

RESULTS AND DISCUSSION:

A comparison of (>99.999%w/w) pure lead with that of lead-1.25% antimony alloy shot shows a radical difference in corrosion rate (**FIGURE 1**). The pure lead leachate reached a maximum concentration of 1.58mg/Litre within 50 days and no apparent increase after 100 days. We projected a maximum corrosion rate over the period but this would likely be an overestimate and ignoring any consequence of a build of lead carbonate on the shot surface. Under field conditions that achieve encapsulation, this phenomena causes preservation of lead artefacts. The higher rate of corrosion calculated would likely prevail under conditions where the lead shot was constantly exposed to percolating acid rain with as would occur in light sandy soils which do not favour build up of stable alkali corrosion product. These conditions are typical of many older shooting ranges. In comparison the alloy shot fared badly. Its corrosion rate ($\text{mg/m}^2/\text{day}$) was projected at more than 22 times that of pure lead. This was deemed significant, even allowing for possible error in determining surface area, estimated at circa +/-5%. The increased rate was expected owing to the presence of antimony and its Redox interaction with the lead. What was a surprise was the relative rate of corrosion.

FIGURE 1



The phenomenon of antimony accelerating lead alloy corrosion has been known in the battery industry for very many years. Antimony is employed to give the grids of battery plates, hardness and strength. Also, it improves castability by giving better contraction qualities and fewer flaws. Lead alloys with up to 11% antimony have been employed but these batteries had a propensity to ‘self discharge’ and exhibit antimony induced corrosion of positive plate. The components of modern lead acid batteries are constructed with differing levels of antimony. Positive plates are made from only 2% antimony to minimize self discharge and reduce the grain size of the internal micro-crystalline structure and some batteries use lead-calcium alloys to eliminate antimony altogether and thereby greatly extend battery life. Trends of lead usage should be of particular concern to ammunition makers, as secondary or recycled battery lead is the primary source of ballistic lead. There may a tendency for secondary lead producers to supply ammunition makers with lead grades that are deemed unsuitable for the battery market by virtue of their trace metal content. Ammunition makers buy lead on its ballistic qualities do not necessarily specify other trace metals such as silver which may adversely impact the corrosion properties of spent projectiles.

FIGURE 2

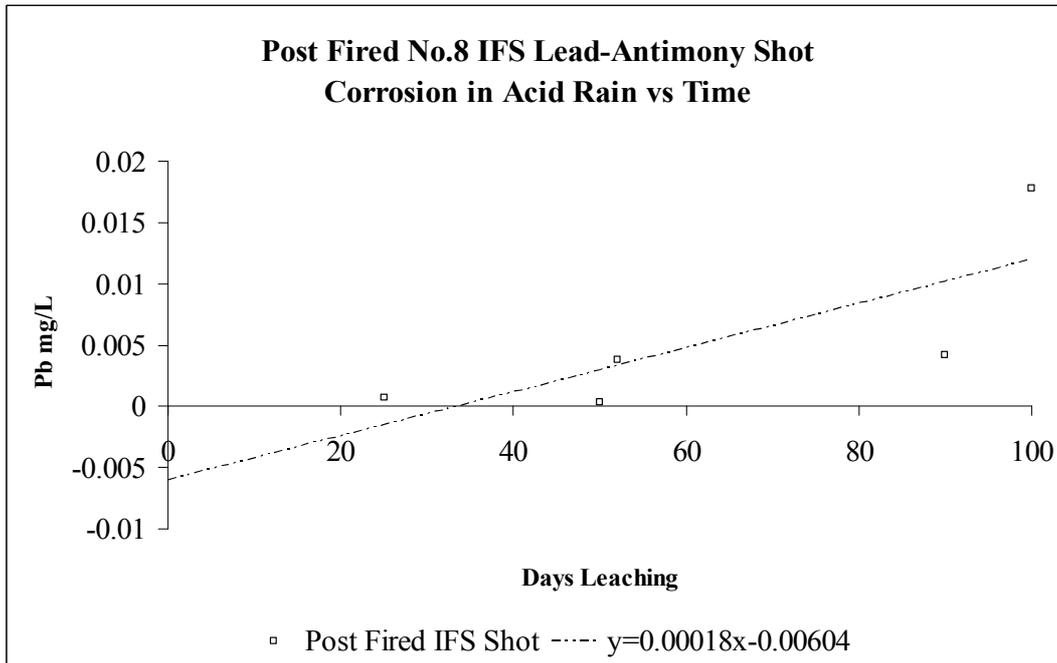
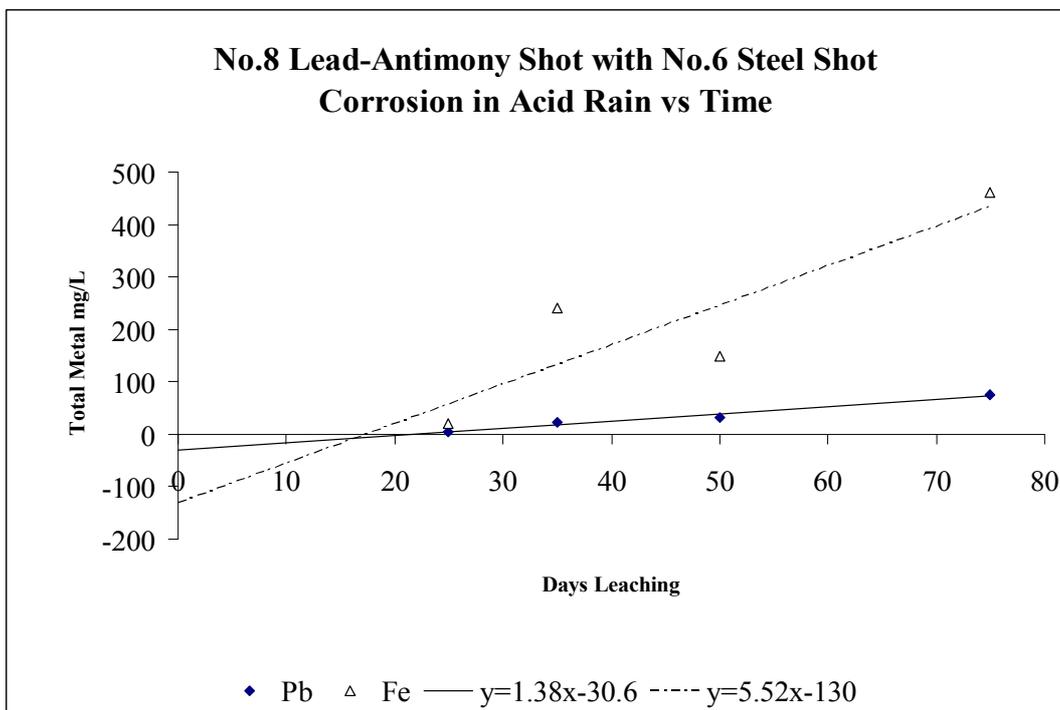
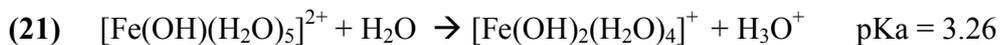


FIGURE 3



Redox reactions are impeded by a process known as passivation. This occurs where the surface of an electrolytic corroding material becomes saturated with a crust of stable corrosion product. IFS protected shot serves to preserve the surface of the shot from corrosion by covering the surface with a Redox stabilised metal sulphide layer. Even firing and impact scared areas of shot pellets are sealed on exposure of the shot to ground water, post firing and post impact. Comparative leaching results (**FIGURE 2**) show a substantively reduce rate of lead bleed. The majority of assayed values were below the normal reporting limit of 0.010mg/Litre.

The comparative corrosion of No.8 lead-1.25% antimony shot in the presence of No.6 steel shot (**FIGURE 3**) gave rise to very low levels soluble heavy metals owing to the powerful sorption effects of the colloidal iron oxides produced by the rusting steel. We were able to determine relative corrosion by monitoring the total dissolved and suspended metals. Dissolved lead did not exceed 22% and was typically <5% of total lead. Total metals indicate that the steel shot corrodes 4 times faster than lead shot. We noted a significant swing in the pH during the course of the experiment. Initially the pH rose to 8.9 within 7 days. Thereafter it dropped to pH 5.1 over the remaining period of the experiment. The acidity increasing proportionately to the amount of iron in suspension. This phenomenon can be attributed to the formation of iron II and iron III oxides. In the early stages of corrosion alkali hydrated iron II oxides (**19**) predominate. With subsequent oxidation, after 2 weeks the acidic iron III oxides (**20**) and (**21**) prevail.



Iron oxide induced swings in pH will have major implications for the management of ranges that allow steel to be fired on lead. Site pH could be anticipated to fall radically. We noted that our lead alloy shot corroded 6.3 times faster due to the presence of iron oxides. We attribute this increase in rate not just to the increasing acidity which only became substantive in the latter days of the experiment but to the Redox Potential of iron III oxide. Iron III is a powerful Redox reagent agent, it has the ability to corrode lead by reduction to iron II, (**TABLE 2**, equation (**15**)). This in turn can rapidly re-oxidise in air to more iron III and thus the reaction would perpetuate. In addition to lead, we noted other heavy metals; antimony, manganese and nickel were present in significant amounts in suspension through sorption to the colloidal iron oxides (**FIGURE 4**). As the majority of environmental regulations pertain to soluble metals this observation might a first sign not appear to be of concern. However: Metals saturated soils will naturally bleed dissolved metal, but under normal conditions sorption to clays, iron oxides and organic material is very strong. M^cLean and Bledsoe⁽⁴⁾ indicate that the principal mechanism identified for lead migration is under conditions of ‘facilitated transport’; lead and antimony sorption to takes place on colloidal sized particles which are easily washed away by heavy rainfall. Fine clays and in particular iron and manganese oxides form colloidal precipitates. Puls et al⁽¹⁰⁾ refer to iron and manganese

as 'Transport Metals'. Therefore, it is clear that addition of steel shot to a site will facilitate migration of heavy metals by providing them with the means to become mobile.

FIGURE 4

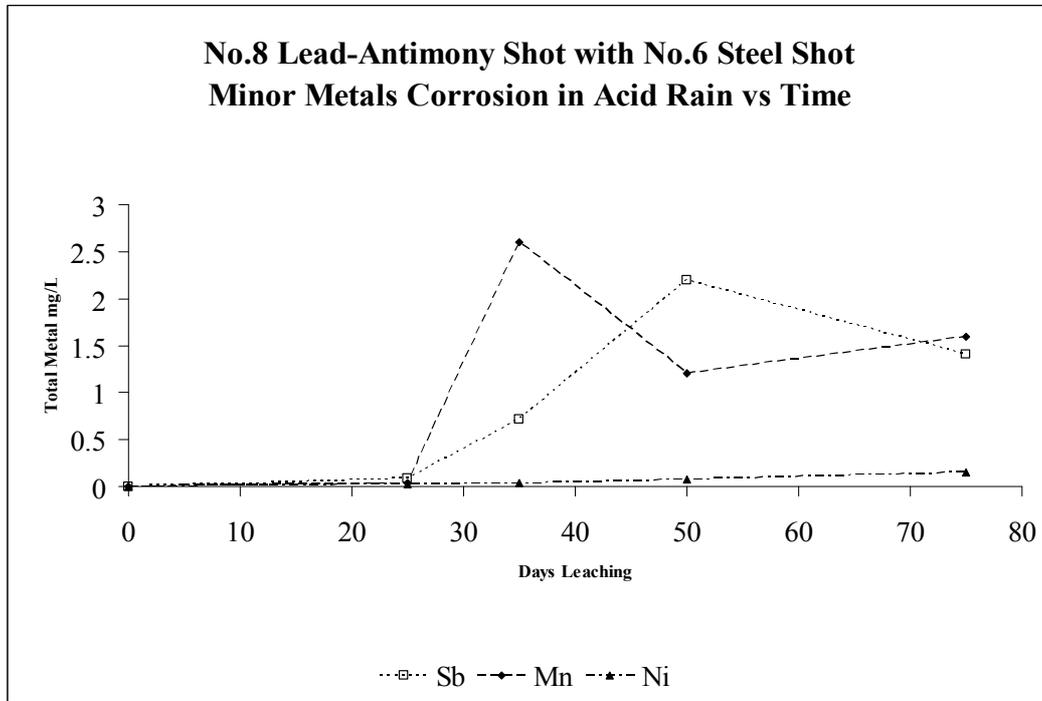
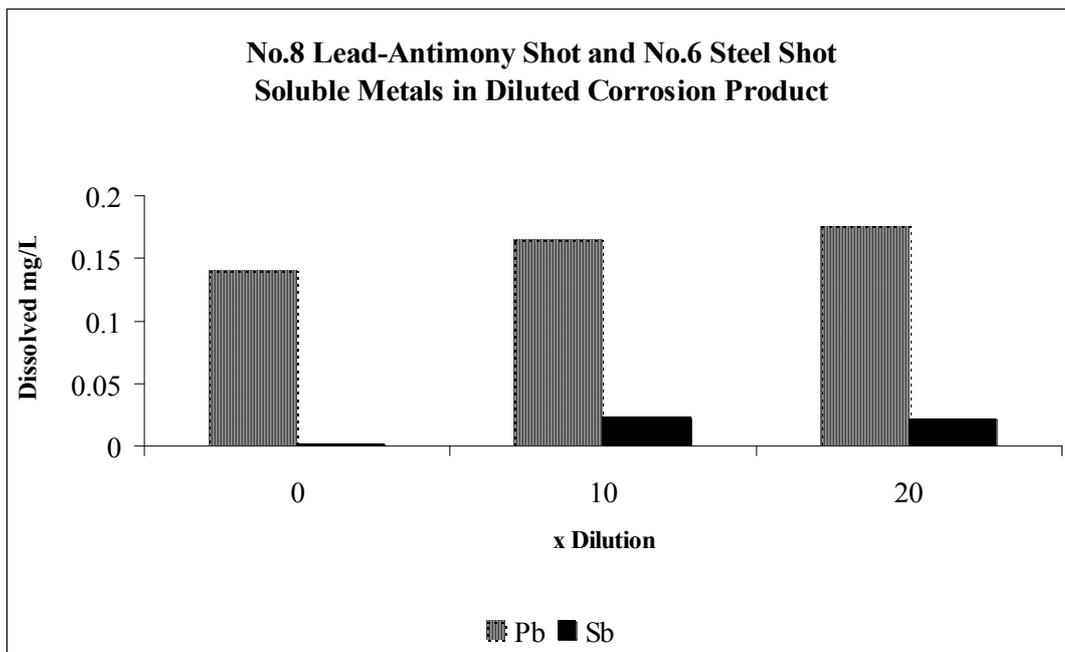


FIGURE 5



To compound the migration problems indicated above is the key fact that metals sorption to iron oxides is reversible. To model the likely impact of dilution post site runoff, we took a portion of the 35 day corrosion product from lead-antimony and steel shot and diluted it further in simulated acid rain at pH 6.4. The undiluted pH was 5.7 and this rose to pH 6.4 and 6.5 when diluted by a factor of 10 and 20 respectively. Despite the pro-rata reduction in total metals we observed an increase in dissolved heavy metals, (FIGURE 5). Iron oxides produced from rusting iron and steel are colloidal in nature. Having sorbed heavy metals, colloidal iron oxides will be easily washed from contaminated sites by rainfall. Having been transported from a high or saturated iron environment these iron oxides can easily dissolve and in doing so release their toxic cargo of heavy metals. Therefore, not only do iron oxides accelerate the corrosion of lead-antimony shot, they can also facilitate the migration of lead, antimony and other heavy metals from polluted ranges to deposit this pollution in a soluble form downstream of the contaminated site.

Manganese and Nickel are undesired pollutants. Fine Nickel and many of its salts are SARA 313 listed materials. Manganese if co-administered is known to increase the absorption of lead into the brain by as much as 3 times, with a consequential increase in toxic effects ⁽¹¹⁾. Furthermore the co-occurrence of lead and manganese pollution as evidenced by the US Toxic Release Inventory has been implicated as the second biggest factor influencing rates of juvenile delinquency and criminal violence after drug addiction and alcoholism in parents ⁽¹²⁾.

Rooney ⁽¹³⁾ claims that arsenic, copper and chromium pollution arise from the corrosion of lead shot in range soils. Our 'soil free' studies do not indicate any significant release of these elements. However, minor contaminants such as arsenic, copper and chromium may actually originate from previously immobile minerals in the range soil and be rendered soluble through the actions of corroding ammunition materials with high Redox potentials ⁽¹⁴⁾. Probably the best advice that can be given to prevent heavy metals migration would be not to provide the contaminated site with any high Redox potential or transport metals, e.g. do not shoot steel shot on a site containing legacy lead.

TABLE 3
Summary of Corrosion Rates for Shot Based on Lead Leaching

Sample	Linear Slope mg/Litre/day	Approx. Corrosion Rate mg/m²/day	Relative Corrosion Rate
Pure Lead (~2mm dia)	0.0129	0.486	0.0447
Lead-Antimony Shot (~2.6 mm dia)	0.228	10.868	1.0000
Lead-Antimony Shot + Steel Shot	1.430	68.163	6.2719
Lead-Antimony Shot + 1% IFS	0.00018	0.0086	0.0008

Electron-microscopy of uncoated lead shot reveals a complex structure. Antimony poor regions appears as granules approximately 10 micron in width by 50 micron in length. These granules are peppered by inclusions of lead oxides and sulphate, revealed as white flecks, (see **FIGURES 6 to 8**). Indications of oxygen content of these regions would imply lead oxide levels of circa 6-12% w/w of the alloy content. The inter-granular antimony rich region (typically >10% antimony) is dendritic and porous in nature.

Post immersion in water, once freshly polished or otherwise exposed lead alloy surfaces are turned black over several days when in the vicinity of the moisture exposed IFS coating. Examination of our polished cross section of IFS coated shot post 3 days immersion in water reveals (**FIGURES 10-12**) a crystalline deposit of predominantly lead sulphide with other accompanying elements from the IFS coating. This passivating scale covers the entirety of the exposed surface showing that ballistic surface damaged to the initial coating can be sealed post firing when exposed to ground water thereby reducing the potential for lead corrosion.

CONCLUSIONS

Our corrosion rate results (**TABLE 3**) show that lead –1.25% antimony alloy corrodes 22 times faster than pure lead in acid rainwater. Furthermore, this corrosion is significantly accelerated (6.3 times) by iron oxides produced by co-corrosion of commercial steel shot. Comparable studies of ‘post fired’ Integrated Fixation System (IFS) protected lead-antimony shot showed significant stability to acid rainwater. Expected lead shot corrosion times of circa 10,000 years in temperate regions and >1,000 years in tropical regions have been cited in the literature ⁽¹³⁾. Our studies suggest that given a surfeit of acid rain, pure lead shot might last over 21,000 years, commercial lead-1.25% antimony alloy shot would survive only 1,200 years and in the presence of high amounts of iron this would reduce to 190 years. By contrast the corrosion rate of the IFS protected shot implied a corrosion time of circa 1.49 million years

Our studies indicate the firing of steel shot onto ranges containing lead shot will; adversely influence site pH, accelerate lead corrosion and provide a ‘transport metal’ which will facilitate migration of lead, antimony and other heavy metals from the contaminated site, depositing them into solution further downstream. Furthermore commercial steel shot gives rise to manganese and nickel as additional undesired pollutants. The presence of manganese in particular is known to magnify the toxic effects of existing lead pollution ^(11,12).

Contrary to the field observations of others, we do not observe significant arsenic, chromium or copper pollution directly emanating from corrosion of commercial lead or steel shot. However, there is a significant body of literature which suggests that secondary pollution can occur due to the Redox influences of commercial shot corrosion products on soils already containing otherwise insoluble heavy metals minerals.

We conclude that IFS protected projectiles could significantly reduce lead corrosion on ranges. Alternatively, shooting cleaner lead would be less harmful than shooting steel onto legacy lead containing soils.

The main implication of this report is that any change to the materials of ammunition construction is highly likely to have a major impact on the chemistry of range soils. Even supposed inert materials such as tungsten, TNI and other speciality nickel-steels currently under evaluation as ammunition materials can be anticipated to exhibit redox interactions with existing soil pollutants and background metals minerals. The author believes that some of these alternative materials have been promoted as 'non-toxic' and 'inert' materials for range use without thorough environmental evaluation of their chemical nature and the ecological consequences. By contrast, the shooting of purer or 'better' lead and/or IFS corrosion protected lead offers a viable and environmentally sound alternative.

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FIGURE 6

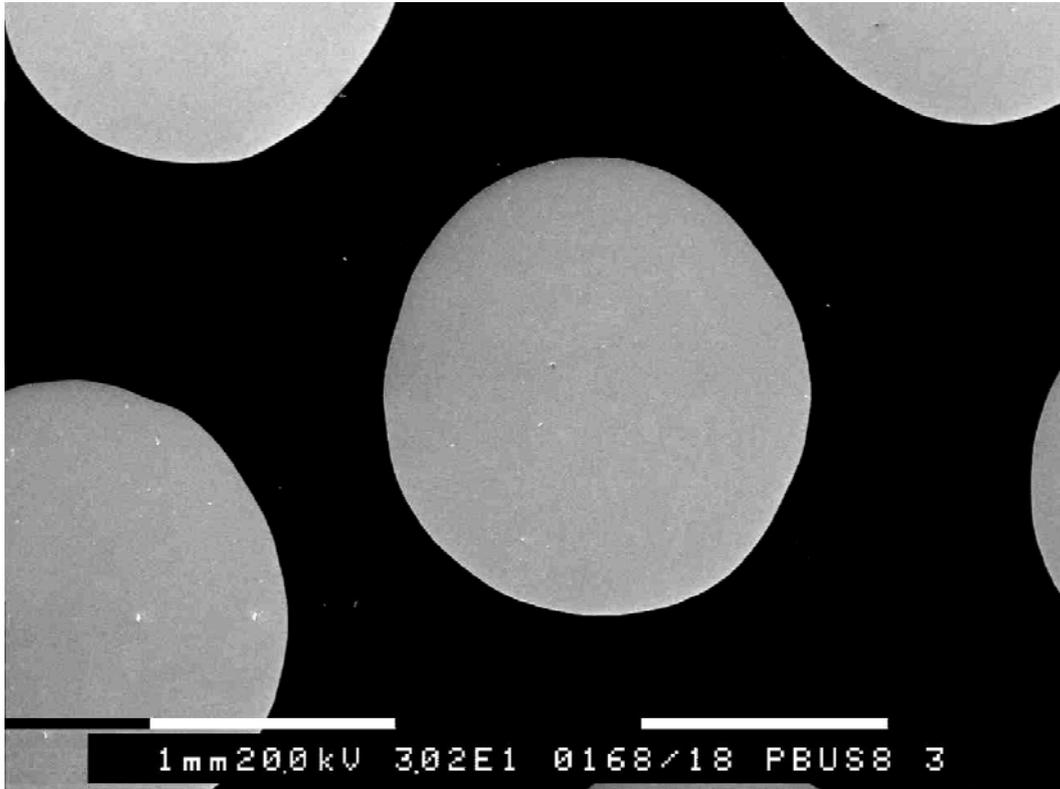


FIGURE 7

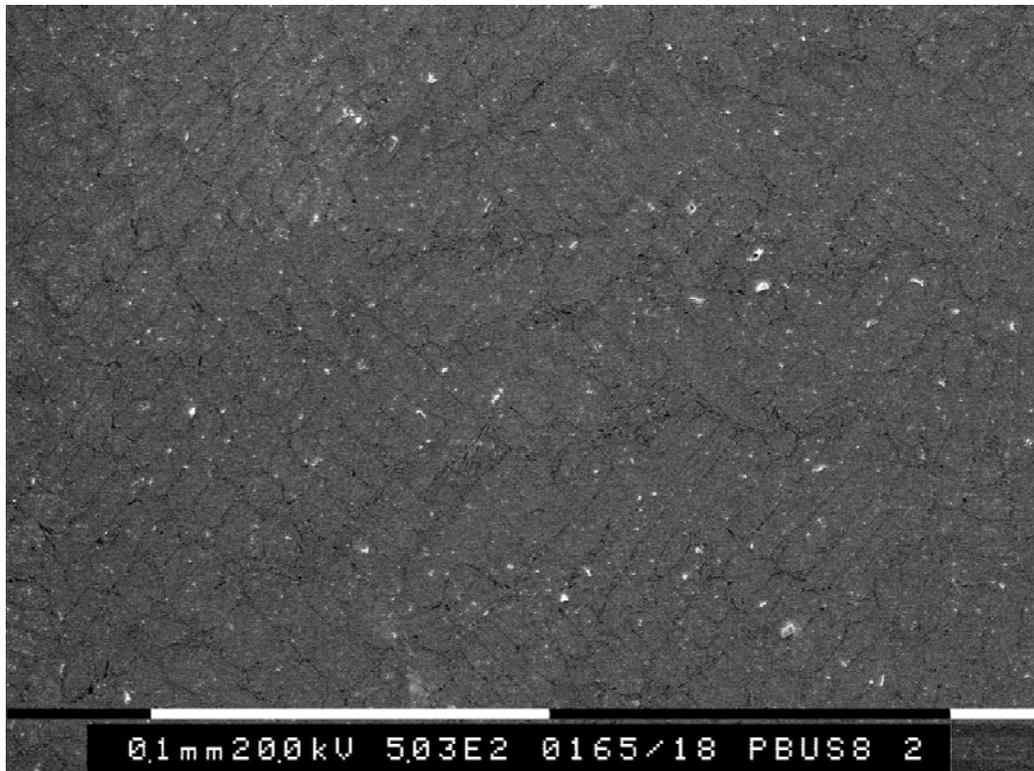


FIGURE 8

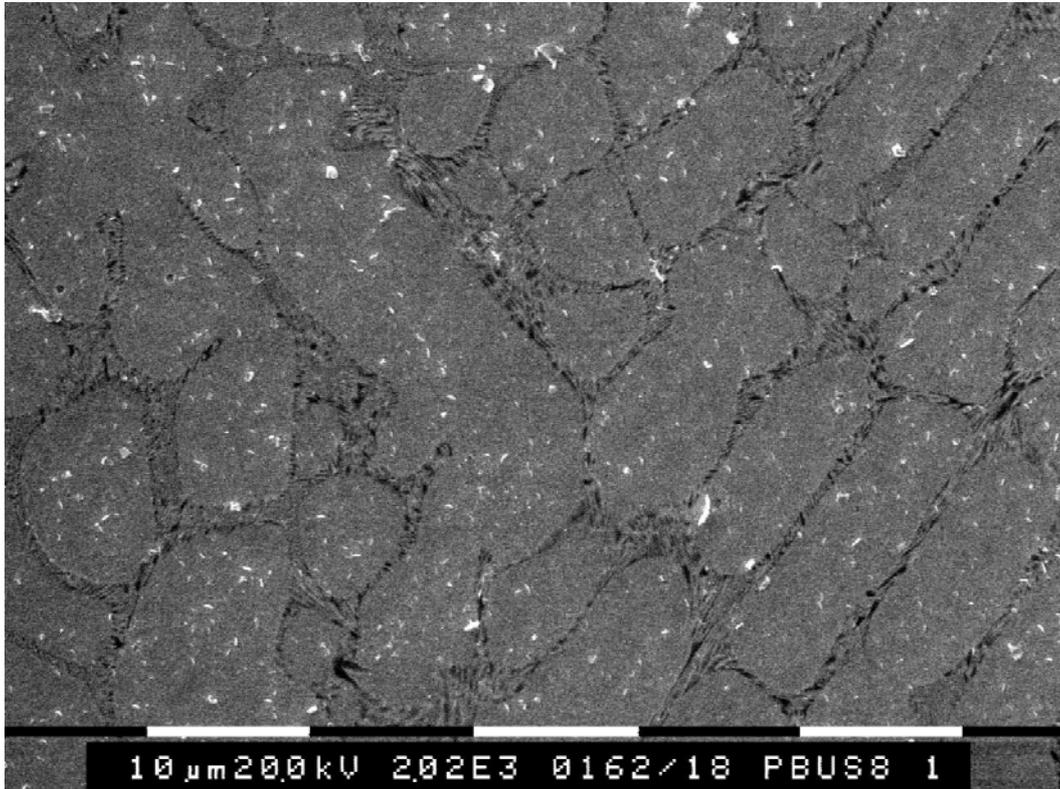


FIGURE 9

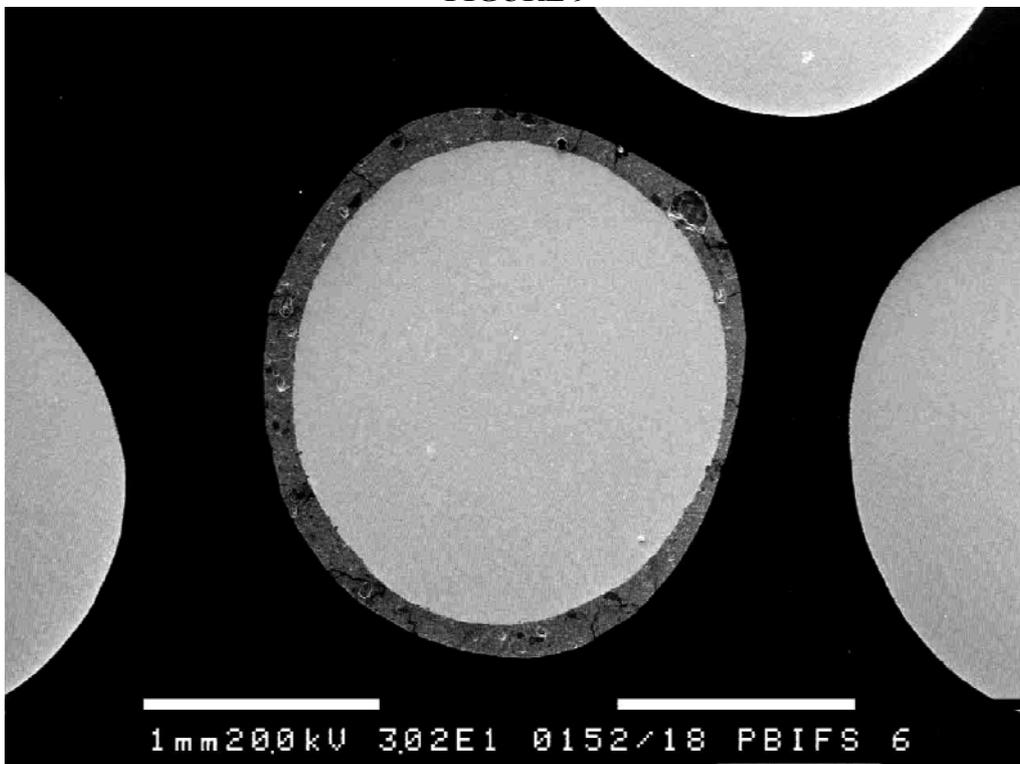


FIGURE 10

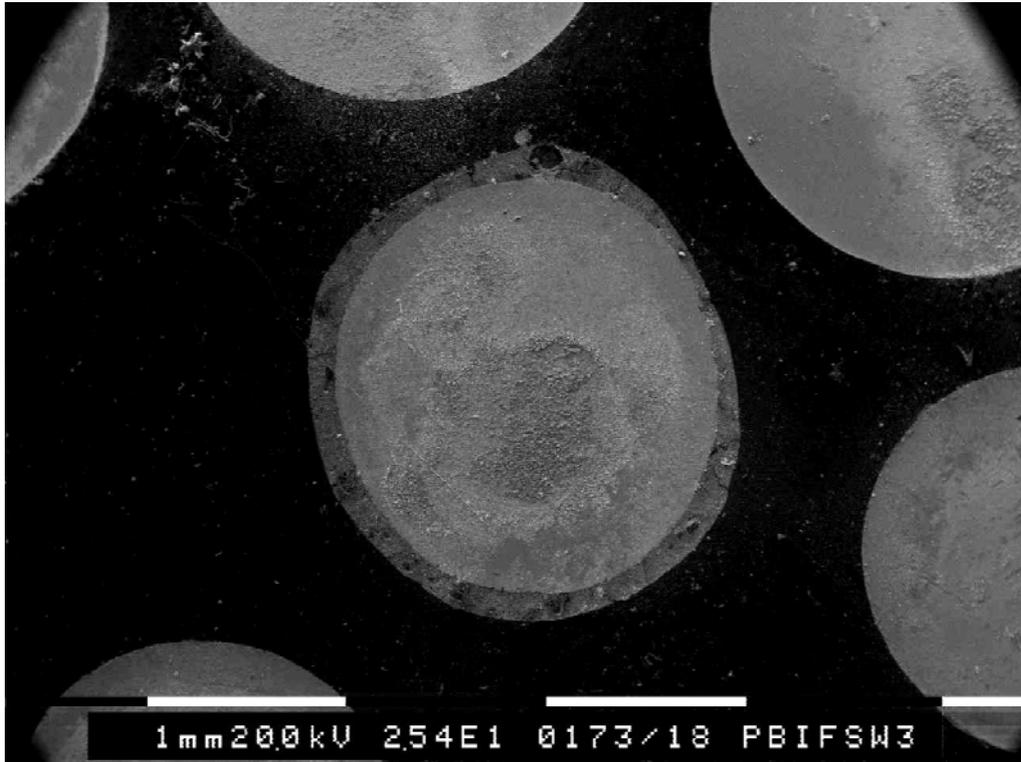


FIGURE 11

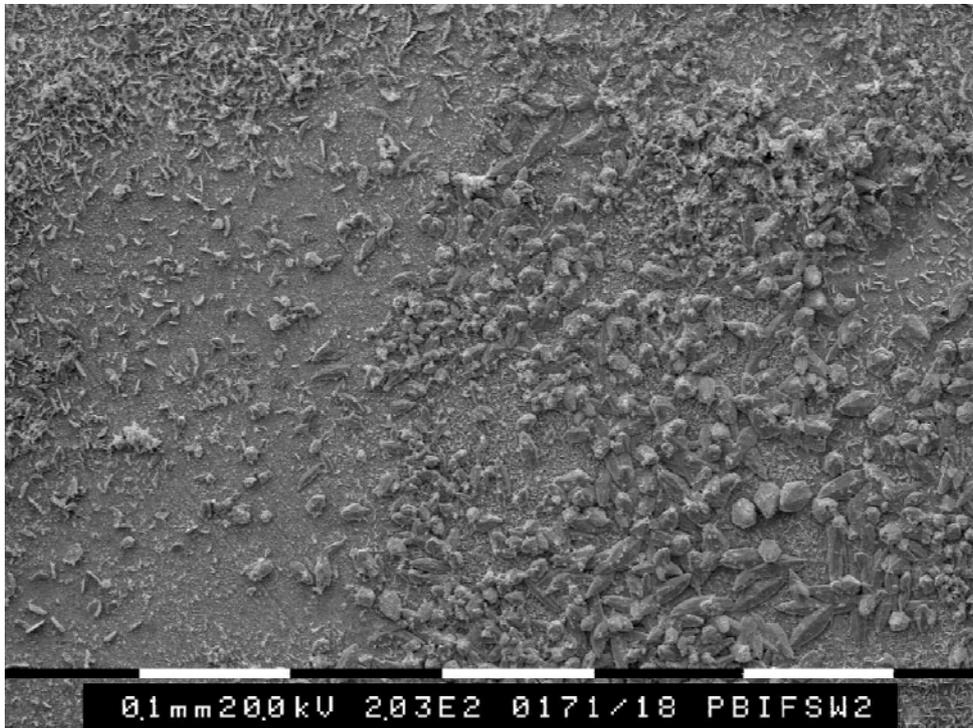


FIGURE 12

