MEETING THE NEEDS OF TOMORROW: A BREAKTHROUGH TECHNOLOGY FOR PRODUCING LEAD METAL

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The Doe Run Company, in partnership with Engitec, has developed a proprietary new technology expected to revolutionize the lead industry. The breakthrough technology improves lead processing efficiency and dramatically reduces air, land and water releases. The process replaces lead smelting in high-temperature furnaces with a contained, wet chemical process that recovers up to 99 percent of the lead contained in mined concentrates. This paper provides a brief overview of the new process and discusses the expected benefits, illustrating how the lead industry can take a dramatic step forward with the application of this promising technology.

INTRODUCTION

Conversion of lead ore into useful metal and alloys has been accomplished through a high temperature smelting process that has evolved very little in more than 100 years. The Doe Run Company, in partnership with Engitec, has developed a proprietary new technology that is expected to revolutionize the lead industry. The breakthrough technology not only improves lead processing efficiency, but it also dramatically reduces air, land, and water releases.

Essentially, the technology takes lead metal production from "fire to water" in a process that replaces existing pyrometallurgical production technology with a contained, wet chemical process that recovers up to 99 percent of the lead contained in mined concentrates. The process also eliminates nearly 99 percent of process releases to air, land, and water.

Combined with emerging battery and electric vehicle technologies and other energy storage applications, this hydrometallurgical technology can help achieve the shared goals of a cleaner environment, economic vitality, smaller carbon footprint, and reduced dependence on imported metal.

This paper provides a brief overview of the new process and discusses the expected benefits, illustrating how the lead industry can take a dramatic step forward with the application of this promising technology.

NEW PROCESS DEVELOPMENT

As the largest integrated lead producer in the Western Hemisphere, The Doe Run Company has a long-standing interest in technology to improve the performance and efficiency of production. Doe Run is based in St. Louis, Missouri, a state rich in lead-bearing ore with a long history of mining and lead metal production.

Doe Run's goals for any process to convert lead concentrates to finished metal include:

1) provide a high recovery rate for metal from lead concentrates, greater than 96 percent;
2) achieve Doe Run's high-purity product standards, 99.99 percent pure lead;
3) ensure cost competitiveness;
4) meet and outperform current and future anticipated regulatory standards; and

5)develop a process that delivers on community and societal expectations for lead metal production in the 21st century.

Doe Run evaluated the commercially available alternatives and concluded they could not meet these goals.

Recycling Technology
Doe Run recycles lead-acid batteries using a process developed by Engitec Technologies S.p.A. Today, Doe Run operates one of the world's largest battery recycling facilities and recycles 13.5 million batteries every year. This supports the battery industry's comprehensive battery recycling program, virtually a closed-loop process that makes lead a recycling success story unmatched by any other material.

New Lead Technology
In the early 1990s, Doe Run and Engitec again partnered to explore the development of an efficient and emission-free technology for the production of primary lead from lead sulfide concentrates. The resulting patented hydrometallurgical process is currently referred to as the Doe Run technology.
In simple terms, the new technology uses a wet chemical process to selectively dissolve lead concentrates into solution and then extracts lead from the solution using an electric current. This electrowinning process is similar to the technology commonly used to extract zinc from concentrates.
However, it has never been used successfully in a commercial application for primary lead production.

Technology History
Commercial hydrometallurgical production of zinc began in 1915 and a similar process has been used for copper since 1967. However, the zinc process also employs a pyrometallurgical component as zinc sulfide concentrates are "roasted" to create a metal oxide. Both the zinc and copper processes use sulfuric acid to dissolve or leach the metal oxides into a solution. The metals are subsequently electroplated in a low-voltage cathode-anode cell reaction through the process of electrowinning. The sulfuric acid hydrometallurgical processes used for copper and zinc cannot be applied to lead because lead is not soluble in sulfuric acid.

Intensive research on the hydrometallurgy of lead was undertaken in the 1970s and 1980s, without successful process development. In the early 1990s, the historical research was extensively studied by Doe Run's technology partner, Engitec. Based in Milan, Italy, Engitec is a leading global engineering firm with a 70-year history in non-ferrous metals production.

Technology Breakthrough
The breakthrough came when the partners identified a fluoborate electrolyte as a potential technology to recover high-purity lead with significant operational advantages over alternative processes based on ferric chloride (Olper et al., 1993). Doe Run and Engitec embarked on a significant program to jointly develop this method and determine its commercial feasibility shown schematically in Figure 1. Since the first pilot plant was established in the 1990s through the current demonstration plant operation, the partners have accumulated more than 200,000 hours of engineering, design, and operating experience.
The Doe Run technology is fed by lead sulfide concentrates without a high-temperature pretreatment to create an oxide. Doe Run is not aware of any other all-inclusive hydrometallurgical technology for the production of lead metal from concentrates being used anywhere in the world. The Doe Run technology is highly efficient; recovery of lead directly to a finished product is approximately 99 percent, compared to 95 percent with traditional smelting.

Technology Development
More than a decade later, the development of this new process has entailed laboratory development and testing, design, construction, and operation of a pilot plant, and design and development of a demonstration plant. Over the last four years, more than $30 million has been invested in the demonstration plant, engineering studies, and design of a commercial-scale processing facility.

The current step in the delivery of the project is a detailed feasibility study and final engineering of the commercial-scale plant. Along with the feasibility study, Doe Run is evaluating possible locations for a commercial plant and alternatives for financing the new facility. The process is being designed in a modular fashion that will allow capacity to be added as warranted by demand. Preliminary cost estimates for a unit with an annual capacity of 60,000 tons exceed $100 million.
The Doe Run technology is covered by process patents in the United States and a number of other industrialized countries. Doe Run and Engitec jointly own the intellectual property and Doe Run currently has an exclusive license to the technology.

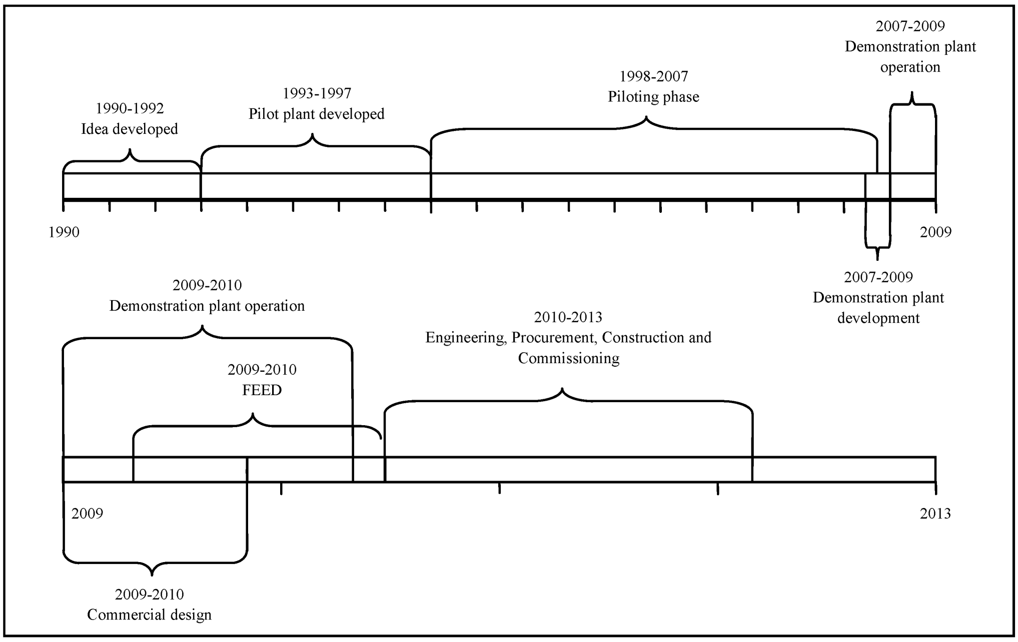

Figure 1 – Timeline of research, development, and commercialization of Doe Run technology

PROCESS DESCRIPTION

The Doe Run technology process shown in Figure 2 uses four primary steps.

Step 1 – Multi-Stage Leaching/Purification Process Description

In the first stage of the process, lead-bearing concentrate is placed in contact with an oxidizing solution based on fluoboric acid. The leaching unit is a multi-stage, countercurrent unit to maximize extraction of lead from the concentrate and remove impurities. Iron is consumed in the process and other impurities are precipitated. The lead sulfide contained in the concentrate is converted into soluble lead fluoborate and insoluble elemental sulfur.

$$PbS + 2\,Fe(BF_4)_3 = Pb(BF_4)_2 + 2\,Fe(BF_4)_2 + S \quad (1)$$

Step 2 – Electrowinning/Electrolysis

The purified lead-bearing solution from Step 1 is fed to a diaphragm-divided electrowinning cell in which two key electro-chemical reactions take place: 1) plating lead in the cathodic compartment; and 2) regenerating the oxidizing compound in the anodic compartment. In the ideal process:

$$Pb(BF_4)_2 + 2\,Fe(BF_4)_2 = Pb + 2\,Fe(BF_4)_3 \quad (2)$$

The diaphragm is a filter cloth designed to prevent the oxidized iron compound produced in the anodic compartment from being retro-diffused in the cathode compartment, which would reduce process efficiency. The pore size of the diaphragm is calibrated to ensure that the flow of electrolyte from the cathode side to the anode side is high enough to overcome any counter-flow of iron; this key factor also governs energy consumption. The configuration is simple, easily handled, and very efficient in electrochemical performance.

Step 3 – Co-Product Collection/Re-Leach

In the third step, sulfur contained in the residue is leached and subsequently recovered through precipitation, thus making the remaining residue available for further processing to recover other metal coproducts.

Also in this step, the small portion of unrecovered lead from the initial leaching in Step 1 will be treated through a re-leaching process that will recover 75 percent to 80 percent of the remaining lead. This solution will then be returned to the electrowinning circuit for plating. This brings the recovery of lead metal in the overall hydrometallurgical process to 99 percent.

Step 4 – Bleed Treatment

In the fourth step, the minor metallic impurities that leached into solution in Step 1 are precipitated and removed from the solution. Metals (Me) dissolved in a concentrated fluoboric acid solution will precipitate when sulfuric acid is added, so impurities are removed and the fluoboric acid they consumed in the leaching step is regenerated:

$$Me(BF_4)_2 + H_2SO_4 + x\,H_2O = MeSO_4.xH_2O + 2\,HBF_4 \tag{3}$$

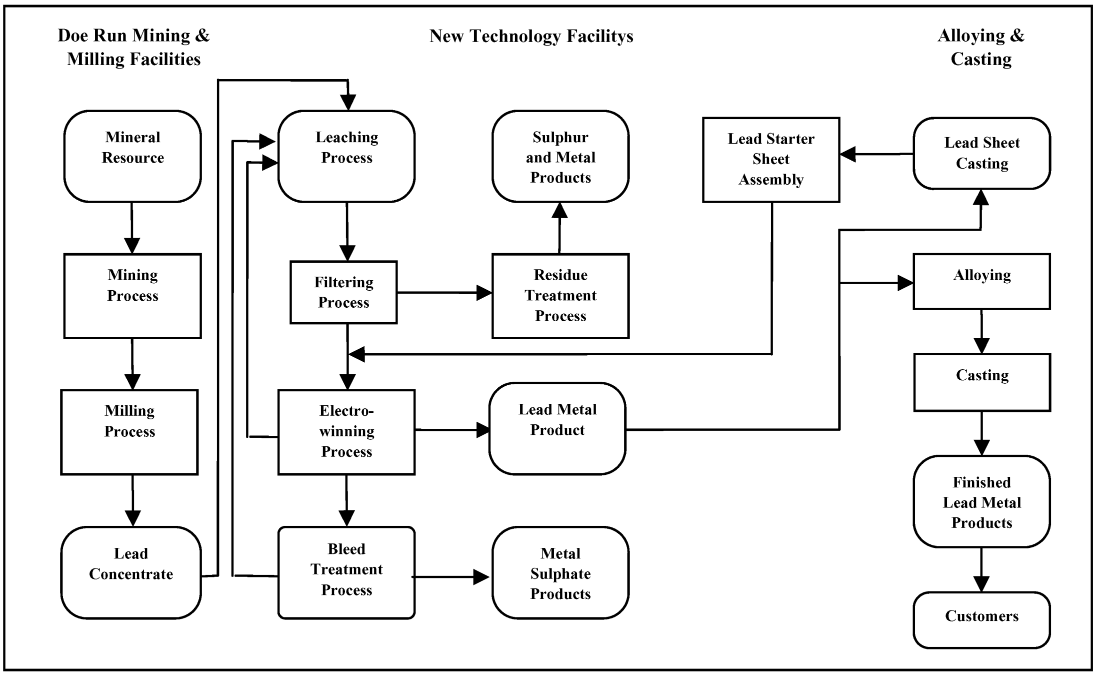

Figure 2 – Schematic diagram of Doe Run technology for producing primary lead from ore

BENEFITS OF NEW TECHNOLOGY

The Doe Run technology would represent the first commercialization of a process that Doe Run expects will transform the way primary lead metal is manufactured around the world. It would contribute to the extended viability of the significant ore reserves that gave rise to the U.S. lead industry and ensure a continued role in serving a growing world market for lead.

Lead plays a vital role in startup and motive power for vehicles, including the latest hybrid and micro-hybrid vehicles. Lead-acid batteries also provide backup power for hospitals and cellular and computer networks. Lead shielding is used for protection in medical and nuclear power applications. Lead is also expected to play an increasing role in energy storage for renewable energy production technologies.

Implementation of the new technology offers a number of advantages, including a reduced carbon footprint and significant reductions in process releases to air, land, and water of nearly 99 percent.

Smaller Carbon Footprint

The pyrometallurgical technology for converting lead sulfide to lead metal operates at temperatures in excess of 900 ºC (1,650 ºF). This requires large amounts of energy and results in the production of greenhouse and other anthropogenic gases. In contrast, the hydrometallurgical process operates at relatively low temperatures below 100 ºC (212 ºF).

Lead also is highly suitable for electrowinning because it has one of the highest electrochemical equivalents. As a result, energy consumption per pound of lead production is approximately 25 percent of the energy required for copper and only 15 percent of the energy required for zinc (Olper, 1998).

Compared to the current pyrometallurgical process, the Doe Run technology reduces the energy required per pound of products produced by approximately one-third.

Environmental Benefits

The Doe Run technology drastically reduces environmental releases, including air, water, and solid waste, that are associated with traditional technologies. Because the new process uses no furnaces, no gaseous effluents containing sulfur dioxide and particles have to be controlled and scrubbed. No acid plant is required and solid wastes also are minimized.

Solid Waste

Unlike traditional pyrometallurgical smelting, the Doe Run technology does not produce slag, a granular, glass-like byproduct. Doe Run's current smelting operations generate more than 50,000 tons of slag each year.

Liquid Waste

Because the process is self-contained, the fluoboric acid activating solution can be recycled back into the process indefinitely. By virtually eliminating process water discharges, permitted water discharges can be reduced by approximately 10 million gallons per year.

Air Emissions

It is projected that the hydrometallurgical process will significantly reduce air emissions of regulated gases, particulates, and lead. Sulfur dioxide regulations adopted by the Missouri Air Conservation Commission in 2009 will require a phased elimination of SO2 emissions at the Herculaneum smelter by 2017. U.S. National Ambient Air Quality Standards adopted in 2008 mandate a 90 percent reduction of lead in ambient air, from 1.5 µg/m3 to 0.15 µg/m3, also by 2017. The new technology achieves a reduction in lead emissions of more than 99 percent and virtually eliminates emissions of SO2. In engineering calculations, as confirmed by the demonstration plant, the Doe Run technology meets and outperforms all existing and anticipated air quality standards.

Other Operational Benefits

Because the process generates minimal fumes and dust, improved industrial hygiene is inherent without special protective gear for employees. The process is completely continuous and can easily be automated. Material handling is limited to feeding concentrate at the start of the process and stripping lead metal from the cathode.

The output of the process is high-purity refined lead, 99.99 percent pure. Engitec also has identified various ways to produce the necessary quantities of fluoboric acid lixiviant for commercial production at reasonable cost using relatively common materials such as hydrofluoric acid, boric acid, sulfuric acid, calcium fluoride, calcium borate, and fluosilicic acid (a byproduct of phosphate fertilizer manufacturing).
The hydrometallurgical plant is modular and scalable, making it relatively economical to adjust for increases in capacity. In comparison, the larger capital investment required for pyrometallurgical processes makes them economically viable only with large-capacity units.

Sustainable Supply for Strategic Applications

Lead-acid batteries account for 80 percent of today's lead consumption, and are expected to require an increasing share in the future. As shown in Figure 3, the share of lead devoted to batteries has tripled in the last half-century.

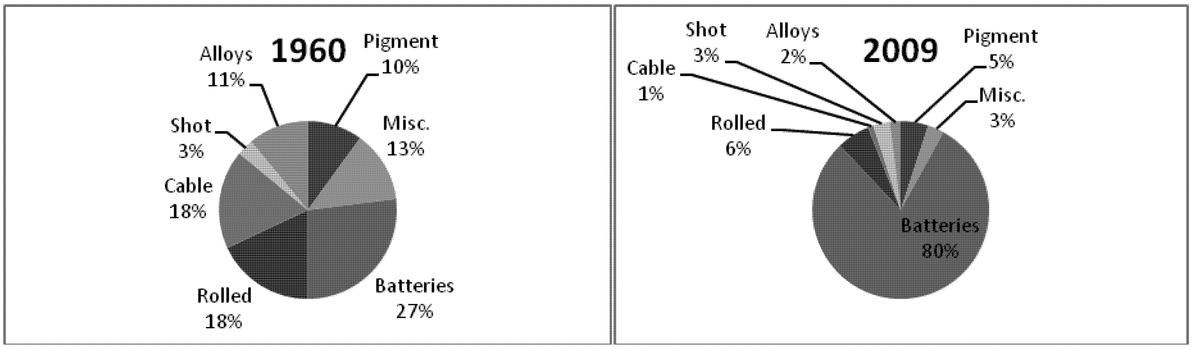

Figure 3 – Growth in share for batteries as uses of lead evolved (Anonymous, 2010)

A common use is the battery for starting, lighting and ignition (SLI) in gasoline and diesel-engine vehicles, including hybrids. Lead-acid batteries also power electric vehicles like forklifts, golf carts, and e-bikes, and play a major part in backup power for hospitals, telecommunications, and computer networks.
Other batteries are used for aerospace and defense products, including aircraft, tactical vehicles, and submarines. Lead-acid batteries also are at the forefront of storage technologies for renewable and green energy, such as solar cells and wind turbines. Moreover, storage of spent nuclear fuel and construction of new nuclear generating facilities in the future will continue to require lead shielding.
Doe Run supplies its customers with lead metal and more than 50 customized alloys for these strategic applications. Doe Run technology enables production of lead metal at a competitive cost with lower emissions. Sustainable domestic processing and supply will reduce pressures toward offshore sourcing with the attendant environmental benefits of reduced transportation, including reduced fuel consumption and emissions.
Both Doe Run and its customers recognize the value of maintaining a reliable and sustainable domestic supply. The company enjoys close relationships with its customers, including partnerships to develop alloys that meet specific product requirements. These relationships are long-lived; in one case, the strategic business partnership extends back 58 years.
Customers representing a significant portion of Doe Run's lead sales have formally recognized Doe Run's efforts to develop this new technology and the important contribution it represents for their business and North American manufacturing facilities.

CORPORATE CITIZENSHIP

The Doe Run Company has a long history in the communities where it operates. Many of these communities grew up around Doe Run facilities, or those established by predecessor companies, more than a century ago. Doe

Run contributes to the economic vitality of these communities by providing safe, high tech employment, which are some of the best-paying jobs in the region. The company is also a major taxpayer and both the company and its employees are active participants in community life. As a corporate citizen, Doe Run has a long history of improving its environmental performance. Air emissions have decreased by 92 percent since 1981. Implementation of the new Doe Run technology would further reduce impact on neighbors and employees. While worker occupational exposure to lead is maintained within guidelines of the Occupational Safety and Health Administration (OSHA), the new technology would further improve the environment within manufacturing facilities and the surrounding community.
Missouri already is home to the most productive lead mines in the United States. With higher efficiency, the Doe Run technology can extend the useful life of these mines, enhancing the economic vitality of local communities.
Doe Run's considerable efforts to ensure a sustainable future for primary lead production in North America have been well received by key audiences, including regulatory authorities as well as legislative and community leaders and North American metal customers.

THE ROLE AND REPUTATION OF LEAD

While much popular attention is devoted to electric vehicles and new battery technologies, lead-acid batteries continue to play an important role in current vehicles, both those powered by conventional internal combustion engines and hybrid-powered vehicles. It is likely lead-acid batteries will continue to meet needs for starting, lighting, and ignition power for the foreseeable future. Indeed, automotive applications are expected to account for the bulk of the overall growth in demand for lead, from 8.5 million tonnes in 2009 to 10.4 million tonnes in 2014 (Anonymous, 2009).

Batteries for Hybrids and Electric Vehicles

The International Lead-Zinc Study Group has determined that the future of batteries for hybrid and pure electric vehicles is heavily dependent on the cost and availability of batteries with high energy and power densities, short charge times, and a long life (Anonymous, March 30th, 2010). Even the most advanced hybrid vehicles, such as the Toyota Prius and the Chevrolet Volt, include a lead-acid battery along with their other technologies.
In spite of the increasing sales and marketing of electric vehicles, their technology still has major hurdles to overcome. A March, 2010 survey from Accenture (Motavalli, 2010) indicated that 65 percent of respondents would buy a hybrid or electric vehicle as long as it doesn't sacrifice benefits of conventional vehicles and some 55 percent said they didn't want to pay a premium price. Yet, current electric battery cars cost more than comparable conventional models and in many ways deliver less (Motavalli, 2010). The combination of higher cost and performance limits for all-electric cars mean that conventional internal combustion engines and hybrids will retain a dominant role for some time to come.
Contrary to general perceptions, over the next 10 years the development of micro-hybrid and hybrid vehicles are more likely to have a positive impact on the demand for refined lead metal than to result in a reduction in usage. In the longer term, any impact on the usage of lead remains dependent on major scientific advances in fuel cell and/or non-lead battery technology. Even in the event of a breakthrough, raw material supply issues would have to be overcome in the case of both lithium and nickel-based battery technologies (Anonymous, March 30th, 2010).

Advanced Lead Acid Batteries

Doe Run is a founding member of the Advanced Lead Acid Battery Consortium (ALABC), which was formed in 1992 to pool resources from more than 50 battery manufacturers and their suppliers to improve the design, construction, and performance of lead-acid batteries to help electric vehicles become a reality. Through these efforts, ALABC has demonstrated that the workhorse lead-acid battery system still belongs in the race with newer technologies.
The consortium completed a 100,000-mile test drive of a Honda Insight with lead-acid battery power. This demonstrated that lead-acid is at least as durable as nickel metal hydride, as well as more efficient and

considerably less expensive. ALABC and Doe Run's customers continue to develop stored energy products that have the necessary performance characteristics to meet society's needs at a cost that is much lower than competitive technologies.

Importance of Lead's Reputation

The most immediate challenge facing the lead industry today is the negative character attached to the image of lead. However compelling the technical data, there remains a risk that society will choose less-effective technologies to store energy if lead's reputation obscures the many benefits of lead itself and the industry's ability to produce lead without negative impacts on the environment.

As noted earlier, recycling of lead automobile batteries in the United States is virtually a closed loop process. Data from the U.S. Environmental Protection Agency indicates more than 99 percent of auto batteries are recycled, more than twice the recycling rate of aluminum beverage cans (Anonymous, March 24^{th}, 2010). The energy required to recycle lead is much less than aluminum or steel, for example, which limits greenhouse gas emissions and the overall carbon footprint.

It is important for the lead industry to effectively communicate the technical advantages of lead as well as the positive contributions recycling and technology can make to a sustainable supply. In this respect, the Doe Run technology can contribute even more than a cleaner and more efficient production process. This technology has the potential to set a new standard for sustainable lead production around the world. By helping to transform the lead industry, it can improve the public perception of lead and help perception match the reality of the important role lead plays in the quality of life for millions of people.

REFERENCES

Anonymous, "Advanced Lead-Acid Battery Consortium, 2010-2011 Prospectus", Advanced Lead-Acid Battery Consortium, Durham, NC, 2010.

Anonymous, "Global Lead Concentrate Market to 2020, 2009 Edition", Brook Hunt, Chertsey, Surry, 2009.

Anonymous, "The Potential Impact of Hybrid and Electric Vehicles on Lead Demand", International Lead and Zinc Study Group, ILZSG Insight, No. 30, March 2010, 3.

Anonymous, "Municipal Solid Waste Generation, Recycling, and Disposal in the United States: facts and Figures for 2008", US Environmental Protection Agency, Solid Waste and Emergency Response, retrieved from http://www.epa.gov/wastes/nonhaz/municipal/pubs/msw2008rpt.pdf on March 24, 2010, 3.

Motavalli J., Seven Barriers to the Electric Car, BNet, retrieved from http://industry.bnet.com/auto/10004151/six-barriers-to-rapid-ev-penetration/ on March 24, 2010.

Olper M. and Maccagni M., "The Production of Electrolytic Lead and Elementary Sulphur from Lead Sulphide Concentrates," Hydrometallurgy: Fundamentals, Technology, and Innovations, J.B. Hiskey and G.W. Warren, Eds., Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO, 1993, 1147-1167.

Olper M., "Fluoborate Technology – A New Challenging Way for Primary and Secondary Lead Processing," Zinc and Lead Processing, J.E. Dutrizac, J.A. Gonzalez, G.L. Bolton, and P.J. Hancock, Eds., The Metallurgical Society of CIM, Montreal, QC, 1998, 185-198.