

# DTSC TECHNOLOGY COLLABORATION PROPOSAL INITIATIVES RD2017008 AND RD2017009



**EXPLORATION & DEVELOPMENT  
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**July 7, 2017**

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<sup>1</sup> Figures are labeled with the date of July 7, 2017. These are the same figures from the paper drafted in April 2017.

## 1. BUSINESS CASE

In California, approximately 32 million vehicles on the road are utilizing lead batteries for starting, lighting, and ignition. Annually, approximately 12-16 million of these lead batteries need to be recycled.

The ‘spent’ lead batteries are recycled to reclaim lead metal and plastics to be used for new lead batteries. This recycling process, which takes place around the globe, utilizes pyrometallurgical (high-heat) smelting and refining.

The fundamental principles of pyrometallurgical smelting and refining have not changed significantly for over a hundred years. The pyrometallurgical smelting and refining process separates lead metal from other metals and impurities, creating various air emissions. The majority of these emissions are captured through a variety of emission control technologies but, as regulatory standards change, emission controls often need to be replaced with newer technologies with the risk for some facilities being that emission control technologies do not exist to allow them to continue operating.

Years of research by The Doe Run Resources Corporation (Doe Run) and Engitec Technologies, SpA (Engitec) has recently culminated in a revolutionary new technology - Flubor. The Flubor process replaces pyrotechnology by utilizing a hydrometallurgy process with a proprietary solution. Lead is placed in the solution and is then plated on cathodes through an electrowinning process. This technology has the capability to revolutionize and transform the way lead metal is recovered around the world. California has an opportunity to take part in this revolutionary transformation by having the first commercial plant constructed in the state.

With virtually no air emissions emanating from the new technology, the process is protective of human health and the environment. Furthermore, the activating solution, fluoboric acid, can be recycled and reused indefinitely within the process. Additionally, the unique process operates without the need to discharge process water.

The Flubor process was first conceptualized for the recovery of lead paste from lead batteries. It has since been proven to produce lead metal from lead ore, which is a much more difficult process. This new, proven Flubor process has the following goals:

1. Provide a high recovery of lead metal from lead products (95% of recycled lead comes from ‘spent’ lead batteries and drosses);
2. Achieve Doe Run’s product standard of 99.99% pure lead metal;
3. Maintain cost competitiveness;
4. Meet and outperform current and future anticipated U.S. regulatory standards; and
5. Serve as best available technology to treat all lead-bearing materials.

## **Technology Background: A Full Recovery Process**

The Flubor process has been developed from the bench stage, to the pilot stage, to the demonstration plant stage, to the commercial engineering and design stage. A Detailed Feasibility Study (DFS) for a 90,000 ton per year primary plant was completed by CH2MHill in 2012. The technology has had an independent review by Worley Parsons<sup>1</sup>, which concluded that the Flubor process is ready to be commercialized.

## **The Flubor Process**

The Flubor process is capable of effectively processing primary lead ore, lead metal, or battery paste. The main steps of the process are: sulfidation of paste, leaching, separation of unleached solids, and electrowinning.

Sulfidation of paste is required to prepare the battery paste for the leaching step by converting the lead oxide (PbO<sub>2</sub>) and lead sulfate (PbSO<sub>4</sub>) to lead sulfide (PbS). This is performed by using sodium sulfide (Na<sub>2</sub>S) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Non-lead outputs from this step are water (H<sub>2</sub>O), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), and elemental sulfur (S).

Leaching is performed using a fluoborate ferric solution that is designed to selectively leach elemental lead (Pb) and lead sulfide (PbS) into solution. Secondary lead can be fed directly as lead metal. Battery paste can be fed after sulfidation. The lead is dissolved into solution as lead fluoborate. One key aspect that sets the Flubor process apart from other technologies and enables a more pure electroplated lead is the selectivity of the fluoborate ferric solution; other elements are not leached in any appreciable quantities, thus enabling a more pure lead product. A second key aspect of the Flubor process is that the fluoborate ferric solution can be regenerated and sent back to the leaching process for reuse, which minimizes waste compared to other hydrometallurgical technologies.

Electrowinning is accomplished by applying electricity to the lead-rich solution, which plates the lead metal onto metal cathodes. After leaching, the lead rich solution is pumped to the electrowinning cells where high purity lead metal (99.995%), in sheet form, is produced. By producing lead metal in sheet form, the Flubor process has an advantage over other hydrometallurgical processes, which typically create lead powder or granules at lower purities that require further refining and inefficient melting resulting in more emissions and dross wastes.

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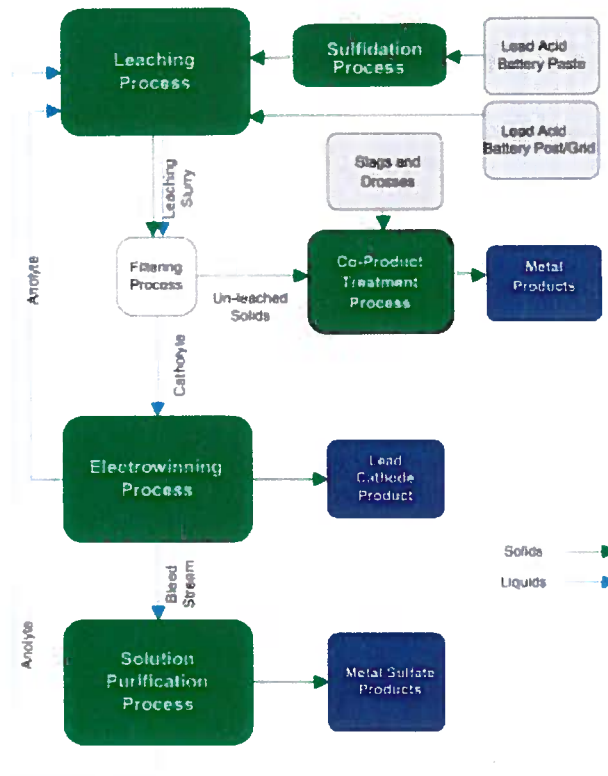
<sup>1</sup> Started as Wholohan Grill and Partners, an Australian engineering consultancy, acquired Worley (American based engineering firm strong in off shore gas and oil in 1987), acquired Parsons E&C based in Houston, TX in 2004 a global leader in hydrocarbons and strong reputation in Power, Oil, Gas, Refining, Petrochemicals and Chemicals sectors globally which had separated from Parsons Corporation based in Los Angeles, CA. After which the company changed its name to Worley Parsons ([www.worleyparsons.com](http://www.worleyparsons.com)). They have 157 offices in 43 countries and 35,600 employees.

**Figure 1.1 Hydrometallurgy Process Flowsheet**

DTSC Technology Collaboration Proposal

The Doe Run Company

July 7, 2017

**Non-Lead Product Recoveries: Doe Run's Proprietary Chloride Technology (Co-Products) Process**

Doe Run has independently developed a second technology, the Co- Products process, to recover non-lead products from the Flubor process. As discussed above, the leaching step of the Flubor process is highly selective for lead, leaving other desired metals unleached. The Co-Products process uses a chloride technology to recover other metals, such as silver, copper, antimony, and tin, which can be sold as metal products. The Co-Product process can also process slags and drosses produced from pyrometallurgical technologies or incomplete hydrometallurgical processes.

The Flubor and Co-Products processes, working together, provide for a full recovery of metals when recycling lead batteries. This full recovery of metals reduces the amount of wastes requiring disposal and air emissions when compared to pyrometallurgical processes and other hydrometallurgical processes. At this time, the Co-Products process is at bench scale, but we believe it could be at the demonstration stage within twelve months.

## **Financial**

The Flubor and Co-Products processes are cost-competitive with pyrometallurgical processes. The operating expense for the two technologies is approximately 20 percent lower than a comparatively sized pyrometallurgical plant. It should be noted that the two technologies can also be built separately. The nature of the processes enables the facilities to be built in modular (scalable) units (addition of tanks to the leaching and electrowinning sections) so that production capacity can easily be increased. This flexibility enables a lower investment in capital to begin production while allowing for capacity increases. Pyrometallurgical processes are not able to be built in such a manner due the significant infrastructure required for furnaces.

## **2 PROJECT DESCRIPTION**

The following is a proposal for a project to be undertaken by Doe Run in collaboration with the DTSC. Working in coordination with the Battery Council International (“BCI”), Doe Run proposes to undertake the pilot program described below to further demonstrate the commercial viability of its hydrometallurgical processes. Doe Run estimates that the proposed pilot program will take approximately 18 – 24 months and will result in a final report delivered to DTSC. Assuming the pilot facility is constructed and operated, Doe Run will provide DTSC (or its contractors) with reasonable access to observe and evaluate its operations.

### **Project deliverables:**

1. Doe Run will provide DTSC (or its contractor) copies of most of the studies referenced in the attachment, and access to confidential referenced materials in a reading room in Sacramento for easy access by DTSC (or its contractor), and subject to a confidentiality agreement sufficient to protect Doe Run’s proprietary intellectual property (*e.g.*, confidentiality acknowledgements by reviewers, limitations on note-taking and distribution).
2. DTSC will prepare a report that evaluates the apparent feasibility of the process and appropriateness of further demonstration work. The report could be analogous to those prepared in the past as part of DTSC’s [Environmental Technology Certifications Program](#) or less exhaustive or formal, as DTSC prefers.
3. While DTSC is preparing the report described in item 2, Doe Run will develop a detailed plan for construction and operation of a pilot plant to demonstrate the technology. That demonstration will occur in Viburnum, Missouri, where Doe Run recently has put into operation a state-of-the-art battery breaking facility (adjacent to and feeding an existing pyrometallurgical secondary smelter) from which feedstock for the pilot facility can be obtained.
4. If DTSC concludes that the process is feasible and has the potential to achieve the hazardous waste reduction goals claimed by the company, DTSC will (1) put its



opinion in writing and (2) commit to working with Doe Run to facilitate the construction of the pilot facility, including (if requested by Doe Run) endorsing applications by Doe Run and obtaining loan guarantees or other financial support for construction and operation of the pilot.

5. After Doe Run has completed the plan described in item 3, Doe Run will seek funding for the pilot facility either internally (if business conditions permit) or in the financial marketplace (which may be contingent on DTSC's conclusion per item 4) and confirmation that permits necessary for construction and/or operation of the plant are reasonably likely to be issued.
6. If DTSC's report per item 4 is favorable, it appears that financing can be achieved on commercially-reasonable terms, and permitting issues are resolved on a timely basis, Doe Run will construct the pilot plant.
7. After completion of construction and receipt of all necessary permits, Doe Run will operate the pilot facility for 6 to 12 months. During that period, Doe Run may make adjustments or modifications to the technology.
8. After conducting pilot testing, Doe Run will provide DTSC with a report on the results of the pilot facility operation that is suitable for public distribution.

### 3 PILOT TEST DEFINITION

A pilot test is conducted principally to confirm certain parameters:

1. Efficacy of the proposed process chemistry;
2. The integrity of the process at various through put levels;
3. Testing of various pieces of equipment at a near-to-commercial or at-commercial scale;
4. Quality and marketability of the products produced; and
5. Capital and operating cost estimates.

In a typical pilot test scale-up, the factors of pilot tests to commercial-scale are generally 1/1000, 1/100, and 1/10 as the process is moved toward commercialization. In some cases, the larger scale pilot testing (such as 1/10 scale) utilizes equipment that can be reconfigured into the final process build.

Having spent \$40 million and 20 years developing hydro met processes, with the expertise of our partner company in the fabrication and construction of process plants, Doe Run is confident that we can determine the viability of a process at a 1/1,000 scale pilot test.

Doe Run proposes to undertake this pilot program, capturing synergies with ongoing projects and utilizing our operating plants as raw feed suppliers as well as support facilities. We have extensive mechanical, electrical, and operational capability which is vital when developing new

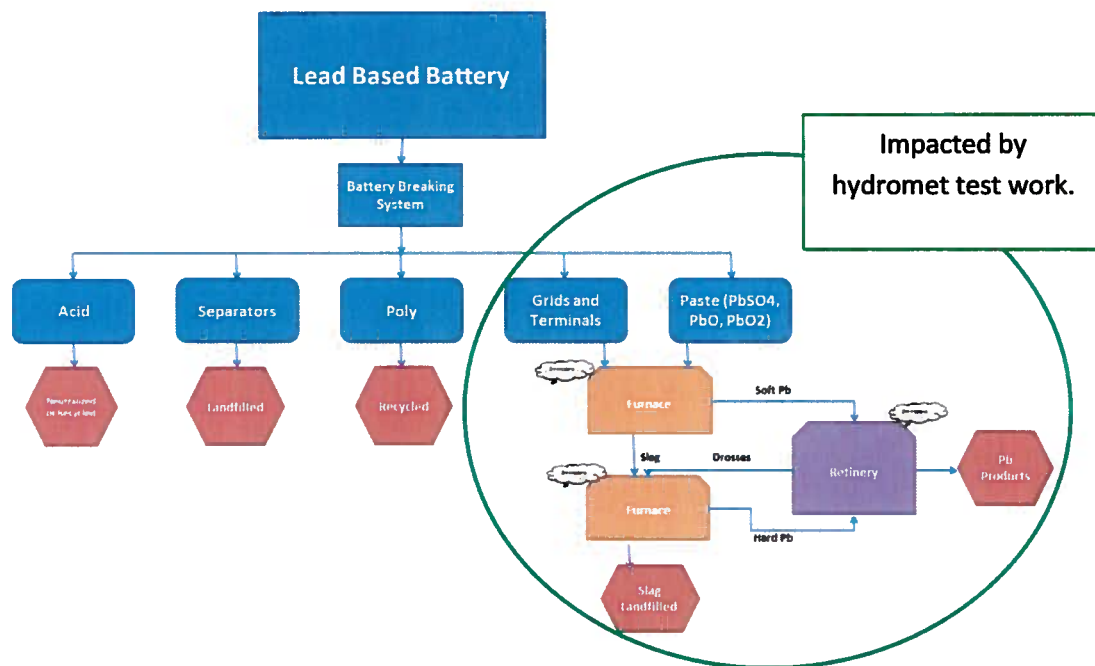


processes and changing test configurations. Our BRRD recycling facility, one of the largest in the US, produces in excess of 140,000 tons per year of lead (by processing more than 13 million batteries per year) and can provide a virtually unlimited supply of feed stock for the pilot facility.

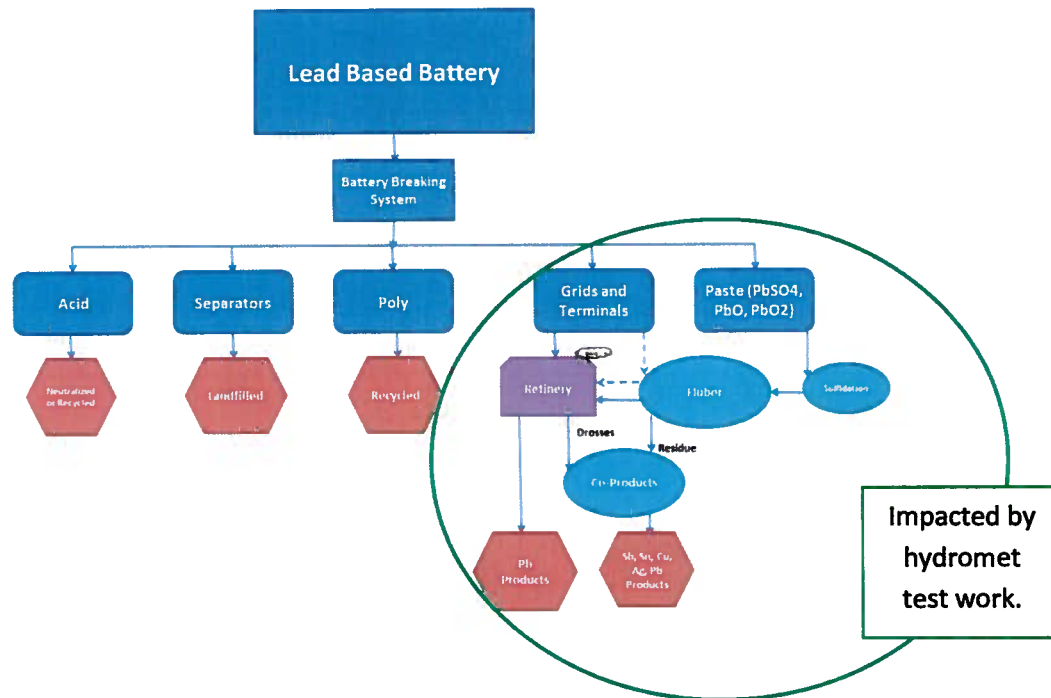
Doe Run is proposing to pilot test two hydrometallurgical methods for the recycling of lead acid batteries. Both of these processes have been developed by Doe Run and are effective at converting various battery components into reusable, high-quality metal products.

The following chart illustrates the current treatment methods for various battery components and identifies those that are the focus of the hydromet processes.

**Figure 3. 1 Current Process Flowsheet**  
DTSC Technology Collaboration Proposal  
The Doe Run Company  
July 7, 2017



**Figure 3. 2 Proposed Process Flowsheet**  
 DTSC Technology Collaboration Proposal  
 The Doe Run Company  
 July 7, 2017



#### 4.1 SOW 1 (CHLORIDE PROCESS)

Doe Run will undertake both bench and pilot scale test work for the Chloride based hydromet process treating the following secondary materials:

- Battery paste
- Pb, Sn, Sb and other dross products
- Lead containing slag.

Stage 1 will be bench scale test work to determine effectiveness of solutions and to develop pilot scale test parameters.

Stage 2 will be the pilot scale utilizing the 50 gal test facility configured for the treatment of the various feed materials.

Stage 3 will be the pilot scale test work utilizing the 150 gal (designed) process.

Total estimated cost for SOW#1 is approximately \$2.0 M. Stage 1 and Stage 2 represent approximately 15% of this cost. This cost does not include feed cost or the cost of Doe Run internal manpower and other internal operating costs.

The estimated timeline for this project will be 12 to 18 months, depending on other project test demands.

Interim stage reports will be generated with a gated process utilized for continuation from one stage to the next.

A final report will be generated outlining the test parameters and significant findings.

## **4.2 SOW 2 (FLUBOR PROCESS)**

Doe Run will undertake both bench and pilot scale test work for the Flubor based hydromet process treating the following secondary materials:

- Battery paste; and
- Battery terminals.

Stage 1 will be bench scale test work to determine effectiveness of feed prep and to develop pilot scale test parameters.

Stage 2 will be the pilot scale utilizing the 300 gal test facility configured for the treatment of the various feed materials.

Total estimated cost for SOW#2 is approximately \$0.4 M. This cost does not include feed cost or the cost of Doe Run internal manpower and other internal operating costs.

The estimated timeline for this project will be 12 to 18 months, depending on other project test demands.

Interim stage reports will be generated with a gated process utilized for continuation from one stage to the next.

A final report will be generated outlining the test parameters and significant findings.

## **5 CONCLUSION**

### **The Future Processing of Lead Batteries and Materials**

The Flubor and Co-Products processes provide a full recovery solution for the recycling of lead batteries in a clean and safe manner and as an economic alternative to existing pyrometallurgical processes or other hydrometallurgical processes. The Flubor and Co-Products processes are the only available technologies that have the potential to achieve all of

the following:

1. Process and recover the lead in a battery (paste, grids and terminals) and return it to new use;
2. Reduce lead air emissions by more than 99% when compared to pyrometallurgical processes;
3. Reduce energy consumption compared to other hydrometallurgical processes due to the lower Kilowatt per hour per tonne;
4. Operate at a low temperature that improves worker safety;
5. Reduce waste streams compared to pyrometallurgical processes and other hydrometallurgical processes;
6. Reduce sulfur dioxide and greenhouse gas emissions;
7. Reduce water consumption and process water discharge;
8. Meet and outperform current and future anticipated U.S. regulatory standards. (This technology does not use blast furnaces, reverb furnaces, rotary furnaces, etc. that are the primary emitters of benzene and 1,3 butadiene. Since the technology does not use these furnaces, the technology does not have these emissions and will outperform the requirements for these air emissions established by South Coast AQMD 1420.1. The technology is a wet based technology and based on testing for lead and arsenic during development of the technology, the process exceeds the existing regulations including South Coast AQMD 1420.1 and based on performance testing to date expected to meet future anticipated regulations.);
9. Serve as best available technology to treat lead-bearing materials;
10. Readily use renewable energy (such as wind or solar) to further reduce greenhouse gas emissions;
11. Nearly eliminate workforce and community exposure to airborne lead and other pollutants; and
13. Significantly reduce the generation of hazardous wastes.

California has the opportunity to take part in revolutionizing the manner in which lead batteries, the most widely used energy storage products in the world, are recycled. This revolutionary new process will meet not only the economic needs of the state, but global desires for cleaner air, land, and water. The Flubor and Co-Products processes should be used to meet the future requirements of today, and tomorrow, for lead metal production by realizing a full recovery of lead batteries.

The Doe Run Resources Corporation welcomes the opportunity to determine how best to bring these technologies to commercialization, in California and elsewhere.

## 6 RESOURCES

1. Definitive Feasibility Study, CH2MHill, July 28, 2011
2. Refining Primary Lead by Granulation-Leaching-Electrowinning, JOM, April 2003
3. A Full Electrochemical Approach in Processing Junk Batteries, Olper, EPD Congress, 1993
4. The Production of Electrolytic Lead and Elementary Sulphur from Lead Sulfide Concentrates, Olper and Maccagni, Hydrometallurgy, 1993
5. CX-EWS: A New Process for the Electrochemical Treatment of the Spent Lead Acid Batteries by Obtaining Electrolytic Lead and Elemental Sulphur, Olper and Morocutti, Third International Symposium on Recycling of Metals and Engineered Materials, 1995
6. Leaching Low Grade Lead Concentrates with the Flubor Process, Maccagni and Pyatt, World of Metallurgy – Erzmetal 2014
7. The FLUBOR Process: Pilot Test Results, Maccagni, Nielsen and Hymer, Proceedings of EMC 2015
8. A Hydrometallurgical Process to produce Zinc from Both Primary and Secondary Sources, Maccagni, Nielsen and Hymer, Proceedings of EMC 2015
9. Recycling Lead and Zinc in the United States, Queneau, Leiby and Robinson, World of Metallurgy – ERZMETALL, 2015