

Recovery of Valuables from Legacy Slag through Innovative Remediation Technology with Ecosystem Enhancement

A proposal submitted to:

Butte Area One
Small Restoration Project

by:

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B. Project Summary and Map:

Title: Recovery of Valuables from Legacy Slag through Innovative Remediation Technology with Ecosystem Enhancement

Sponsor: BNRC

Location: BRW slag and Parrot slag site in Butte Area One

Total Dollar Amount = \$90,247 (BNRC: \$61,342; Montana Tech: \$28,905)

Project Leader: Dr. Courtney Young, Montana Tech

Begin Date: March 01, 2016 (or when funding is in place)

Project Duration: 15 months.

Natural resources are non-renewable and the available reserves of rich primary resources are dwindling. In order to meet ever-increasing demands for mineral and metal commodities, attention has inevitably turned not only to mining low quality ores but also to recycling secondary resources. In the mining industry, one of the most common secondary resources of solid waste materials is smelter slags. Because these resources can be difficult to reprocess, low separation efficiencies result, even when state-of-the-art separation technologies are employed. In this regard, innovative solutions are needed to increase separation efficiencies to optimal and preferably maximum levels. The slags are potential environmental hazards but also sources of valuable commodities. These valuables can be recovered by remediating these wastes while simultaneously restoring affected areas to their previous conditions. With a view to these potential benefits, the present research is proposed in which remediation through technological innovation is accomplished by extracting valuables from legacy wastes and enhance sites to more natural ecosystems.

We propose innovative research focused on advanced processing of slags. Specifically, we will work with Butte Reduction Works (BRW) slag and Parrot slag to develop a unique process for the recovery of zinc, copper, pig iron and glass. A map of the location of the slags is shown in Figure 1. The two slags will first be characterized and then processed by carbothermal reduction either with or without prior matte-phase extraction in order to recover the valuable products mentioned above. Such pyrometallurgical treatments will eventually consume all of the BRW slag in Butte, thereby helping to return an ecosystem to its near-original landscape. All products can be marketed with the glass in particular being made into a key proprietary component for oil production in Montana. Thus, on one hand, the technology developed will help reduce the adverse environmental impact and, on the other hand, recover valuable products. In this case, the ecosystems will be enhanced and significant materials industries may be attracted to Butte.



Figure 1. Butte area one map showing the BRW slag (Courtesy BNRC, 2015).

C. Project Goals and Objectives:

The overall goals of the proposed project are two-fold. First is to extract wealth by recycling the BRW slag and Parrot slag. Second is to restore affected ecosystems to their previous condition. To accomplish these goals, the slag will be treated to generate marketable products. Thus, the specific objectives of the project are:

1. To optimize a novel process to simultaneously separate and recover zinc, copper, pig iron and glass.
2. To illustrate that valuable products can be produced cost effectively. Zinc oxide and copper matte can be sold to the paint industry and base-metal refineries, respectively. Likewise, pig iron can be marketed for steelmaking and the glass can be further processed into a proprietary component for the oil industry.

The ecosystems of the sites will be enhanced by extracting valuables from these solid wastes. Slag removal will enable the restoration of the original landscapes at Silver Bow Creek near Montana Street and the Parrot Site near Civic Center in Butte (see Figure 1). As a result, not only will significant materials industries be attracted to Butte, but the novel technology can be extended to similar applications that exist beyond the borders of Butte.

D. Project Benefits:

The primary benefit of the proposed work is to develop a technology that could lead to the removal of the BRW slag and the Parrot slag within Butte Area One and simultaneously produce marketable products that would help defray costs needed to restore the sites to their near-original landscape. In this regard, adoption of the developed technology will eventually lead to the restoration of Silver Bow Creek and the Parrot Site in this area for public enjoyment once again. The technology development proposed in this work will also be an asset as it can be extended to slag removal and values recovery globally. Consequential to this, a number of other benefits will be realized as itemized below. It is noted that these benefits overlap with the one another but are discussed individually:

- Innovation.** This research will develop innovative remediation technology that is relevant to processing of slags. The technology may be patentable: the pyrometallurgical process for making the products mentioned above, namely zinc oxide, copper matte, pig iron and glass (see Figure 2). Specifically, carbothermal reduction will be performed with or without prior matte-phase extraction. If matte-phase extraction is performed, the valuable products will be zinc oxide, copper matte, pig iron (copper-free), and glass. If matte-phase extraction is by-passed, zinc oxide, pig iron (copper-bearing), and glass will be produced. Research is needed to determine which approach will be preferred.

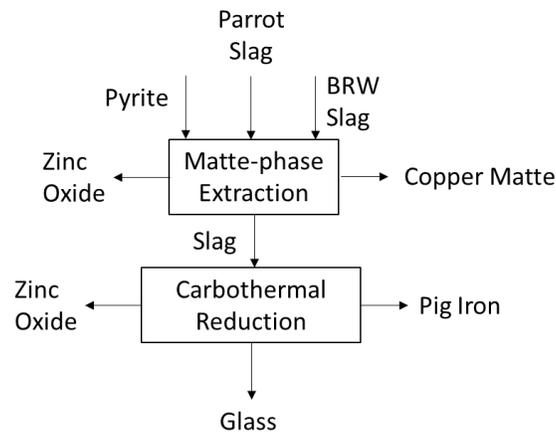


Figure 2: A flow chart of the proposed pyrometallurgical process.

- Scientific Merit.** This approach involves high temperature processing techniques and solves two long standing remediation issues in the city of Butte. It will yield publishable applied and fundamental results that will support significant future funding for materials research.
- Butte Solutions.** Successful completion of the work is sure to attract attention to Butte’s mining, metallurgical and environmental remediation strategies. Slag remediation is a global phenomenon and Butte will be able to provide an effective solution through this research.
- Strong Return on Investment (ROI) for Butte.** ROI will begin with the creation of jobs at Montana Tech and eventually in remediation of the slags leading to the restoration of the ecosystems. Resulting information will strengthen and/or support proposals to NSF as well as Partnerships in International Research and Education. The solution could be extended to other companies generating slag such as ARCO/BP in Anaconda, MT; ASARCO in East Helena, MT; and Stillwater Mining in Columbus, MT. Long-term ROI resulting from the expansion of the scope of solid waste remediation to other relevant industries. Expansion of the scope of this technology to other sectors is likely to bring in more supporting industries.
- Support for Butte’s HR.** By involving the two students in this applied metallurgical research, we will contribute to the development of a high quality workforce.
- Growth of the Research Enterprise.** Successes will not be limited to short term research, long term job creation, and future funding, but also in the improved remediation capacity of Butte and Montana. More efficient production of valuable commodities from the solid wastes and reduction of adverse impacts to the environment through the remediation of slags will both create diverse work opportunities for Butte. Opportunities for further research will increase with additional funding from in-state and out-of-state agencies opening up and enhancing Montana Tech’s research capabilities including avenues of collaboration with other state campuses (e.g., UM Missoula and MSU Bozeman) as well as other regional and global institutions.

E. Project Implementation:

This work will be conducted by five faculty/staff members of Montana Tech: Dr. Courtney Young, Dr. Jerry Downey, Mr. Gary Wyss, Dr. Guojun Ma and Dr. Avimanyu Das. They will supervise one graduate student and two undergraduate students involved in the project work.

The project work will begin with field trips to collect BRW slag and Parrot slag samples. Collected samples will be characterized to evaluate their nature and amenability to pyroprocessing. Processing of the two slags will then be undertaken in two stages. First, matte-phase extraction followed by carbothermal reduction will be performed on the slags to generate the marketable products: zinc oxide, copper matte, pig iron (copper-free) and glass. Second, studies will be conducted using only carbothermal reduction in which case zinc oxide, pig iron (copper-bearing), and glass will be the marketable products. Process parameters such as reaction temperature, time and slag-to-pyrite ratio will be optimized using statistical design of experiments (DOE). Matte-phase extraction will initially be conducted to react copper and zinc in the slags with pyrite to form zinc oxide and copper matte which are recovered and marketed. Iron contained as oxide in the resulting slag is then carbothermally reduced to produce crude pig iron. Statistical DOE will again be employed to optimize the carbothermic reduction process with reference to time, temperature and slag-to-carbon ratio. Under optimum conditions, zinc oxide, pig iron and glass production will be maximized. When matte-phase extraction is used, the copper will report to the matte; and when matte-phase extraction is not used, the copper will report to the pig iron. It is noted that the desired properties of the resulting glass may be a trade-off with the fluxes being considered such that excess sodium and potassium may be needed for glass production in order to maintain low viscosities at low temperatures. On the other hand, excess calcium and aluminum may be preferred for strength. A flow chart of the proposed processing scheme is shown in Figure 2 and the specific tasks are discussed below.

Characterization – The chemical composition and mineralogy of the BRW slag will be available from the ongoing work on this slag by Gammons and Kaplan (2015). Their preliminary results are shown in Table 1. In this regard, the project team will closely interact with Gammons’ research group to make use of their findings in the proposed research and share our findings with them. However, the phases present and their liberation characteristics need to be evaluated from processing perspective. In addition, the Parrot slag and the pyrite must also be characterized. The melting point and the amenability of the two slags for high temperature reduction needs to be established. DTA/TGA, Raman Spectroscopy, ICP-MS and other characterization techniques will be employed to examine the slag samples and the reducibility will be established through detailed characterization. Also, the softening and melting behavior of the carbon as the reducing agent will have to be identified. This characterization component of the research will be conducted by two members, Gary Wyss and Dr. Courtney Young.

Table 1: Preliminary data of the Butte “slagwall” slag (Gammons and Kaplan, 2015, in progress).

Pb, %	As, %	Zn, %	W, %	Cu, %	Fe, %	Mn, %	S, %	Ag, ppm	Ca, %	Si, %
0.094	0.077	2.02	0.095	0.295	27.4	0.217	1.13	16	9.3	18.8

Thermodynamic Calculations – This will be one of the most important tasks in this research. First, the multiphase equilibrium relationships must be determined and then the reduction reactions will be studied thermodynamically. Thermodynamic calculations involving parameters such as change of enthalpy, entropy and

free energy for the reduction reactions will be undertaken to develop a process heat balance and to identify practical windows of operating conditions. These thermodynamic computations will be conducted by the graduate students and Dr. Guojun Ma with oversight provided by Dr. Jerry Downey.

Matte-phase Extraction – A detailed statistical DOE will be the first exercise in this task. The design would involve parameters such as time, temperature, slag/pyrite ratio, and slag/flux ratio. The copper will be recovered in the molten sulfide phase and the zinc will be recovered as oxide. Pyrite addition to the system is required to increase the sulfur content and facilitate capture of these two base metals. Although silver content of the slags is small (see Table 1), it is likely that it will preferentially report to copper matte phase. If the pyrite is gold-bearing, the gold will also report to the matte phase. Suitable flux addition will be investigated in order to make the system more conducive for the recovery of zinc and copper. Dr. Jerry Downey and Dr. Courtney Young will supervise the two students in this stage of the work.

Carbothermal Reduction – In this step, statistical DOE will also be employed to systematically study the influence of time, temperature, slag/carbon ratio, and slag/flux ratio. High temperature furnaces and alumina crucibles will be used to perform the experiments. Carbothermal reduction will normally generate two products: pig iron and glass. If the zinc is not trapped during matte-phase extraction, it will be recovered in its oxide form during this stage. Copper will be recovered in the pig iron. Utmost care will be exercised to improve the properties of the glass product to render it feasible for processing to produce a proprietary component for the oil industry. Of course, the iron in the pyrite will increase the pig iron yield. The work in this stage will be performed by the students and supervised by Dr. Avimanyu Das and Dr. Guojun Ma.

Characterization of Products - The products of the two pyrometallurgical processes will be characterized. The chemical composition and crystalline structure of the products will be determined using Inductively Coupled Plasma mass spectrometry (ICP-MS), scanning electron microscopy with energy dispersive spectrometer (SEM-EDS) and x-ray diffraction (XRD) to evaluate the recovery ratios of valuable elements in BRW and Parrot slags, and the indentation strength of the glassy slag will be determined via Vicker's micro-indentation test to evaluate its mechanical properties. Dr. Avimanyu Das, Dr. Guojun Ma and Mr. Gary Wyss will supervise the work.

Thus, the individual components of the proposed research are listed below:

- Field trip for the collection of approximately 100 kg each of BRW slag and Parrot slag
- Physico-chemical characterization of the slag samples
- Detailed thermodynamic calculations
- Design of experiments
- Matte-phase extraction
- Carbothermic reduction
- Statistical analysis and optimization
- Characterization of all products
- Report preparation and submittal

F. Project Schedule:

This project will commence upon receipt of BNRC approval, which for purpose of scheduling is anticipated to be March 1, 2016. Under this premise, the project will conclude May 31, 2017. The project is broken down into nine activities including the report preparation as shown by the Gantt Chart in Table 2.

Table 2: Gantt Chart showing the individual milestones and the target time frame of accomplishment.

Activity Milestone	Months														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Sample collection	█	█													
Slag Characterization		█	█	█											
Thermodynamic modelling			█	█	█										
Design of Experiments				█	█	█									
Matte-phase extraction					█	█	█	█	█						
Carbothermic reduction						█	█	█	█	█					
Statistical analysis and optimization								█	█	█	█	█	█	█	
Characterization of products					█	█	█	█	█	█	█	█	█	█	█
Report preparation			█			█			█			█			█

G. Monitoring Activities:

- The project team will meet weekly at a minimum to review the progress.
- Internal review meetings will take place at Montana Tech quarterly at the minimum.
- BNRC will be invited to participate in these review meetings.
- Interactions with Gammons’ team will be taken up by the project team routinely.
- Quarterly progress reports will be submitted to BNRC.
- The final project report will be submitted in May 2017.

H. Project Budget:

The total budget for the project is estimated to be \$86,145. This includes a request from BNRC for \$57,790 with a match of \$28,355 from Montana Tech. Details of the budget break up are given in Table 3 below.

Table 3. Proposed Budget for the Research

Category	Expenditure in USD		
	BNRC	Match	Total
A. Salary and Benefits			
Faculty	-	9,728	9,728
Staff	8,840	2,167	11,007
Students	28,800	-	28,800
Benefits	5,434	3,429	8,863
B. Materials, Supplies & Consumables	6,000	-	6,000
C. Contracted Services	-	-	-
D. Equipment	-	-	-
E. Tuition & Fees for Students	-	5,800	5,800
F. Travel	-	2,000	2,000
Total	49,074	23,124	72,198
Indirect cost (25%)	12,268	5,781	18,049
TOTAL PROJECT COST	61,342	28,905	90,247

1. An amount of \$9,728 towards faculty salary (for Dr. Courtney Young and Dr. Jerry Downey) is shown as an in-kind match and is equivalent to two weeks each. A total of \$8,840 is requested for the staff members' salaries from BNRC and is equivalent to four weeks for Dr. Guojun Ma and three weeks for Mr. Gary Wyss for their participation. A match of \$2,167 is also shown as in-kind match from the other staff member (Dr. Avimanyu Das) for his two weeks of engagement.
2. Two undergraduates and one graduate student will be working on this project. The graduate student will be paid \$1,200 monthly during the academic year and \$2,400 during the summer. The undergraduate students will have wages of approximately \$300/month at \$10/hour.
3. Benefits of 3% during academic year and 10% during summer is added towards the students' salaries along with 46% for the staff members' salaries. A match of \$3,429 at 25% for the faculty and 46% for the staff member is also shown against this item.
4. While all the major equipment to execute the project are available at Montana Tech, we will require certain accessories, consumables and chemicals. Heating elements, crucibles, fluxing agents, and characterization accessories will be required at an estimated cost of \$6,000 for the entire project.
5. Waiver of the tuition for the graduate student is matched at \$5,800.
6. The project team will require to make field trips for collection of slag sample. It is also proposed to send the graduate student for a conference on recycling technologies. MT Tech will match all of this amount.
7. IDC's at Montana Tech are 25% of total direct costs.
8. In total, the project cost is \$90,247 out of which \$61,342 is requested from BNRC. The difference of \$28,905 is the in-kind match from MT Tech.

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