The Impact of Physical and Chemical Weathering on Iron Slag from Standish, NY

Maria Leonard (mll15@geneseo.edu), Rachel Kelk, Dr. Dori Farthing
Dept of Geological Sciences, SUNY Geneseo, Geneseo, NY 14454

Abstract

From 1883 to 1907, magnetite ore was smelted at a facility located in Standish, NY. Standish is located in the northeastern region of the Adirondacks. The industrial processing at this site left behind a pile of slag that covers ~13 acres of land. The slag at the site has been classified into 6 broad types based on their physical properties. Exemplars of select types were studied to characterize the impact of physical and chemical weathering on their appearance and bulk chemistry.

The impact of weathering is clearly evident through a comparison of samples collected ~15 years ago to partner samples still out in the field which are more pervasively fractured and coated with calcitic weathering rinds. For more quantitative data on the impact of weathering, we carried out a field experiment and a leaching test. The field experiment entailed exposing different slag samples (glassy, chalky, and massive) from Standish to rain and monitoring the changes in mass over an 8 week period. Each of the three textures lost mass however, the greatest loss came from the glassy sample (1.3% lost). Water that had interacted with the samples was collected. All of the water samples contained particulates and also produced a precipitate from evaporation. This multi-week experiment indicated that both chemical and physical weathering play a role at Standish, but to better understand the role of chemical degradation, we carried out a simple acid leaching test using 2M nitric acid on four samples. All samples lost mass and left particulates in the remaining solution. Bulk chemistry of pre and post test samples was determined by XRF. The chemistry of Standish slag is dominated by SiO_2, CaO, and $Fe_2O_{3(t)}$. A highly vesicular slag showed the largest changes in chemistry (including Ba, V, Zn, Sr, Zr, and Ce) and also changed the pH the most. The other samples showed changes in major elements as well as in Ba, Sr, and Zr.

Introduction

This research aims to study slag from the historical iron smelter in Standish, NY. Slag is a byproduct formed when pure metal is extracted from an ore. Once this processing is complete, the slag is usually dumped into a pile and left to weather over time.

Geographical information about Standish:

•Standish is located within the Northeast region of the Adirondack park in New York.
•The slag pile shown on the map below has an area of approximately 12.8 acres.

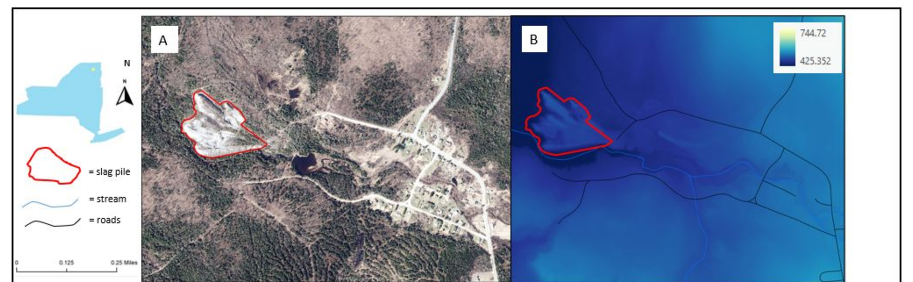

Figure 1 (A): Aerial Photo Map of Standish, NY., 2017 (NYS Office of Information Technology Services).
(B): Digital Elevation Model of Standish, NY., 2016 (NYS Office of Information Technology Services).

Historical Background of Iron in Standish, NY:

1749: Iron ore had been seen by Swedish explorers in the region.
1812-1814: Iron mining and smelting began in the Adirondacks started with settlement.
Mid 1800s: the Adirondacks was one of the top iron regions in the US.
The Civil war, urbanization, and industrialization helped the iron industry remain strong.
Continued expansion of the nation's rail network and the replacement of iron trackage with steel rails created huge new markets.
1883: The Chateaugay Ore and Iron Company had an 8-fire bloomery at Standish (fig. 1,2,3).
1885: The company constructed a blast furnace at Standish to produce pig iron in addition to bloom iron (fig. 1,2,3).
Early 1900's: The industry started to die down Due to nationwide financial struggles.

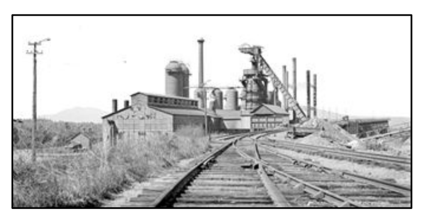

Figure 2: Historical photo of railroad tracks leading to blast furnace in Standish, N.Y. most likely taken from the West facing East toward the pile. (Keller., 1932).

Figure 3: Historical photo of blast furnace in Standish, N.Y. (Keller., 1932).

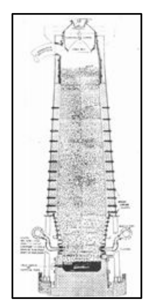

Figure 4: Diagram of blast furnace (Dawson et al., 1988).

Methodology

Figure 5: Photograph taken in 2019 of the partner sample left in the field at Standish, NY.

~15 Year Weathering Study
- Part of a sample of slag was collected in 2005 and the rest was left in the field subject to continuing weathering.
- In 2019 the sample in the field was revisited and compared to the sample in the lab.

Figure 6: Birds- eye view of the 2 month experimental set-up.

2 Month Weathering Study
- A large sample of slag was broken into six smaller samples, weighed, and placed outside for eight weeks, reweighed, dried and weighed again (fig. 10; Table 1).
- Water was collected from beneath the samples at regular intervals over the study period. The water was then filtered and tested for dissolved solids using evaporation.

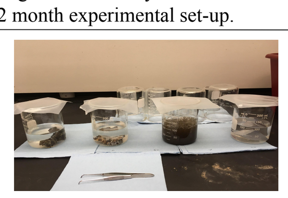

Figure 7: picture of the set up of the acid leaching test

Acid Leaching Experiment
- Four samples of slag types placed in 2M nitric acid for six hours.
- The acid leached samples were chemically analyzed using XRF along with six samples that were not acid leached.

~15 Year Weathering Results

Figure 8a: Photograph taken in 2019 of the partner sample kept in lab conditions in Geneseo, NY.

Figure 8b: Photograph taken in 2019 of the partner sample left in the field at Standish, NY.

- The sample out in the field was more pervasively fractured and coated with calcitic weathering rinds.
- The mineralogy of the slag was determined by XRD to contain predominantly gehlenite, wollastonite, calcite, iron oxides, metallic iron, and organic carbon.

2 Month Weathering Results

- After exposure to weather (e.g. rain and snow) the six samples showed no significant changes in bulk size or shape. However a change in mass was recorded for all samples (Table 1).
- Samples with high permeability from the middle section of the slag (e.g. Massive 1 and 2) absorbed more water than other parts of the slag.
- Dirt and other loose debris was absent from the surfaces of all samples.
- Solid particulates were observed in water collected below all samples throughout the weathering study. These solids were filtered out (fig. 9).
- All water samples, after filtration, produced a precipitate when evaporated. Analysis of precipitates indicate that calcite is the dominant phase.
  - The calcite precipitated as subhedral to euhedral crystals (fig. 11)

Figure 9: Sample of particulates filtered from a single sample of water collected over two weeks. Field of view measures 47mm.

Table 1: Changes in sample mass after the 2 month weathering study.

Samples	Initial mass (g)	Wet mass (g)	Dry mass (g)	Overall % mass lost
Glassy 1	50.41	50.3	50.1	0.61%
Glassy 2	158.84	157.2	156.8	1.28%
Massive 1	52.65	53.8	52.5	0.28%
Massive 2	134.24	135.3	133.7	0.41%
Chalky 1	109.85	110	109.6	0.28%
Chalky 2	78.58	78.8	78.5	0.10%

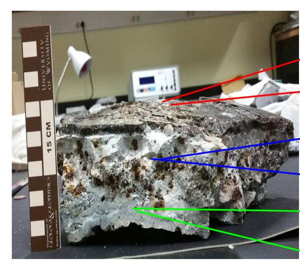

Figure 10: Large slag sample before being broken into the six samples of table 1.

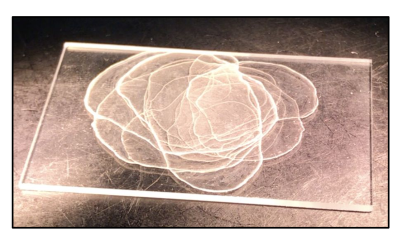

Figure 11a: Precipitate formed by evaporating filtered water onto a standard thin section slide.

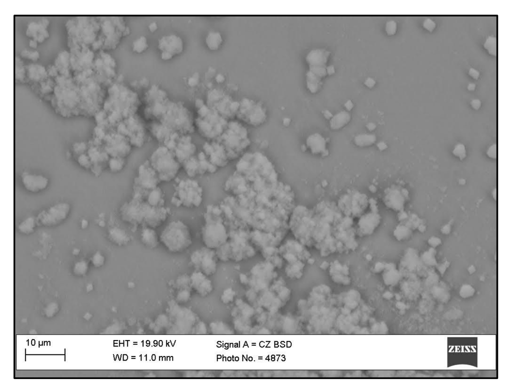

Figure 11b: Backscattered electron image of precipitate shown in figure 11a. Note the euhedral rhoms of calcite in the upper right of the image.

Table 2: Trace element concentrations in ppm for Standish Slag. (Subscript A=acid bath samples; subscript R=rain exposed samples; < indicate concentrations below detection limits)

	Rb	Sr	Y	Zr	V	Ni	Cr	Nb	Cu	Zn	Ba	La	Ce	U	Th	Sc	Cl
Vesicular	39.5	418	49.3	363	12	9	48	6.2	24	198	340	48	83	3.5	20.9	46	554
$Vesicular_A$	31.4	366	56.3	451	19	14	59	6.6	23	114	327	52	106	4.1	25.3	45	599
Glassy	24.7	440	46.5	288	7	4	64	6.3	10	12	246	37	81	2.1	9.8	40	<40
$Glassy_A$	24.1	443	47.3	297	0	5	100	5.7	10	11	243	41	82	2.6	11.5	38	59
Glassy Crusted	37.3	421	45.3	269	56	3	57	6.1	8	11	198	35	85	3.3	18.2	41	60
Glassy $Crusted_A$	38.7	402	44	279	65	5	70	6.7	8	11	206	32	84	4	18.3	38	63
Glassy $Crusted_R$	38.9	427	46.7	273	23	2	60	5.7	6	13	203	45	93	3.4	18.2	38	53
Glassy Crusted (w/o glass crust)	41.5	756	52.9	208	3	5	29	10.1	21	13	1595	40	82	4.9	15.7	41	56
Glassy Crusted (w/o glass $crust)_A$	40.9	605	50.8	245	0	3	57	6.8	7	10	449	41	84	4.3	17.5	42	53

Table 3: Abbreviations used for samples involved in leach tests and XRF chemical analyses.

Code	Sample description
St-G	Glassy throughout
St-GC	Glassy crusted slag
St-B	Massive slag. This sample initially had a glassy crust, but we removed it prior to acid leaching and analysis.
St-V	Vesicular slag
St-NG	Glass-free slag
ST-E	Highly eroded glass-free slag

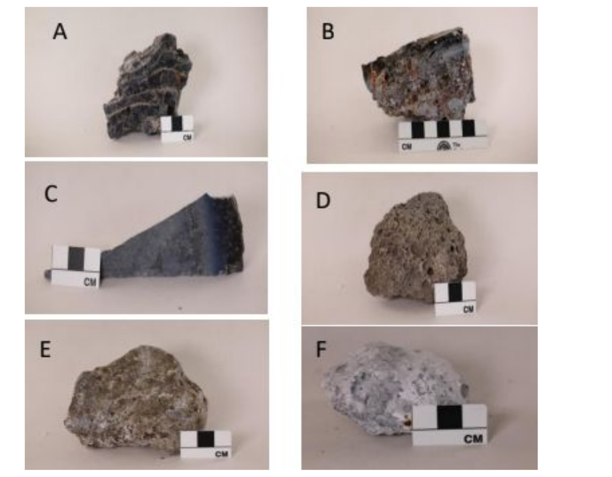

Figure 12: (A) St-G, (B) St-GC, (C) St-B, (D) St-V, (E) St-NG,(F) St-E. All samples were broken up into smaller pieces for testing.

Acid Leaching Results

- The starting pH of the acid was approximately 2.
- After the leaching experiment the pH in each beaker had increased.
  - The St-BA increased the most and the St-GA increased the least.
- The powdered samples of slag after the acid experiment were darker in comparison to the samples powdered before the experiment. (Figure 13)

Table 4: Changes in mass due to leaching experiment.

Sample	Initial mass (g)	Post-acid mass (g)	% mass lost
St-G	21.4	19.5	8.9%
St-GC	21.6	18.5	14.4%
St-V	21.4	14.7	31.3%
St-B	25.8	22.2	14.0%

Figure 13: powdered samples of St-G (pre acid and post acid leaching).

Chemical Results

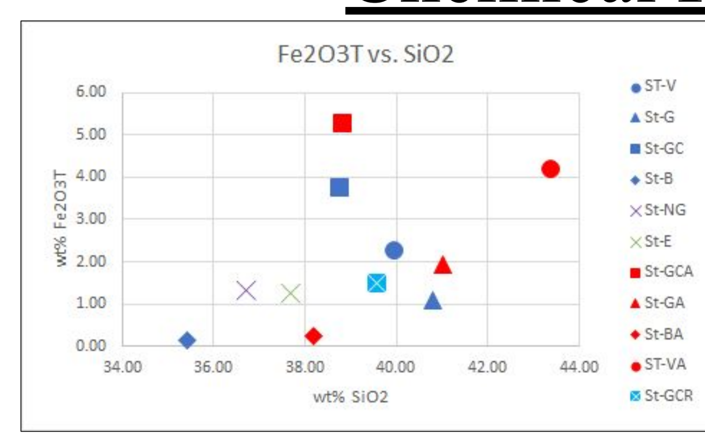

Figure 14: A graph of the wt% of Fe2O3t vs. the wt% of SiO2. A=acid bath samples; R=rain exposed samples

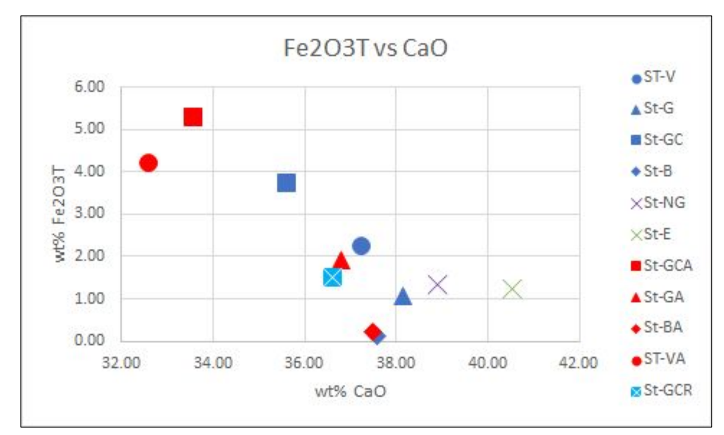

Figure 16: A graph of the wt% of Fe2O3t vs. the wt% of CaO. A=acid bath samples; R=rain exposed samples

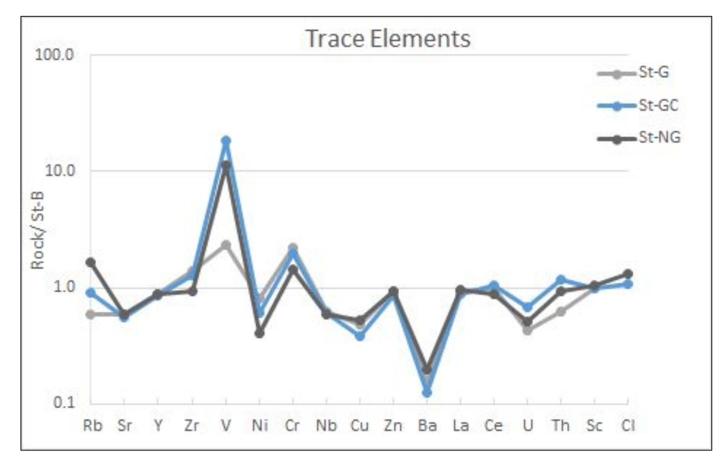

Figure 17: a line graph showing the levels of trace elements of samples in comparison to St-B because it is the bulk slag type.

Major Oxide Observations:
- The biggest changes in Major oxide content after the Acid leaching testing were in SiO_2, CaO, and Fe_2O_3.
- St-GCR doesn't follow the trend of St-GC to St-GCA in major oxide changes.

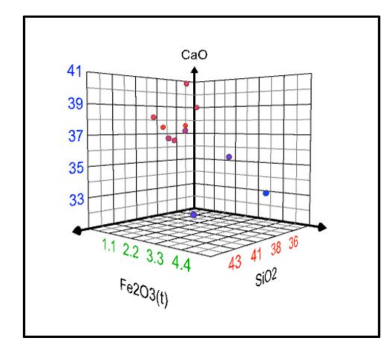

Figure 15: a 3D scatter plot graph showing the wt% of CaO vs. Fe2O3t vs. SiO2.

Observational Summary:

15-year experiment:

After 15 years of sitting out in the elements, the sample exhibited an increase in fractures, white chalky coating (calcite), and oxidation around iron particles. The sample did not change significantly in size.

2 Month Weathering Study:

All samples lost mass though the amount lost was dependent upon sample morphology. The non glassy samples clearly absorbed water during the study so their loss in mass was not apparent until after they had been dried. None of the samples changed drastically in overall appearance other than having loose material on their surfaces "washed" away. Solid particulates were observed in the unfiltered water samples collected from each sample. After filtration and evaporation, a precipitate was observed for each sample. Analysis of the precipitate with the XRD and SEM indicated that calcite is the dominant precipitate phase.

Acid Leaching Study:

All samples lost mass due physical removal and dissolution caused by the acid leaching. All samples increased the pH of the acid though with varying degrees of intensity dependent on sample morphology (the vesicular sample increased the pH the most). The color of the samples also changed due to acid leaching; pre-acid samples were lighter in tint compared to post-acid samples (fig. 12).

Geochemical Data-Majors:

The dominant elements in all slag samples are Si and Ca (all with oxide values greater than 30 wt %). These elements still dominate the leached and rain-test samples. The Si & Ca-rich chemistry corresponds well with the mineral phases identified in the crystalline portions of all slag samples (gehlenite (Ca_2Al_2 SiO_7); wollastonite ($CaSiO_3$); calcite ($CaCO_3$))(Farthing and Sidlauskas, 2006). Acid leaching caused the largest changes in the concentrations of SiO_2, Fe_2O_{3T}, and CaO. SiO_2 and Fe_2O_{3T} tended to both increase in leached samples compared to their unleached partners whereas CaO tended to decrease due to acid leaching.

Geochemical Data-Trace:

The most dominant of the trace elements present in all the samples are Sr, Zr, and Ba (all over 100 ppm; table 2). Ba shows a wide range of concentrations and is more dominant in the bulk massive portions of the slag rather than in the glassy portions. Sr, Zr, and Ba still dominate the leached and rain-test samples.

Discussion

Both physical and chemical weathering impact slag at Standish. Crack formation and propagation is seen throughout the slag pile and we believe it is driven by two processes-frost wedging and volumetric expansion caused by oxidation of pure iron within the slag samples. This region of New York sees significant precipitation and cold weather that are highly conducive to frost-wedging and many of our samples easily absorb water due to primary or secondary permeability.

The primary permeability is associated with a highly vesicular slag morphology that formed when the slag was initially poured onto the dump pile. We associate the secondary permeability with chemical weathering processes of dissolution and oxidation. Our tests clearly show that some of the slag dissolves when it is exposed to an acid. The rain in the Adirondacks is known for its acidity (Driscoll et al., 2002) and when it interacts with slag, it removes material and increase the permeability.

All of the slag samples contain pure iron as either a spherical droplet (prill) or as a concentrated layer. When these particles are impacted by oxidation, the weathering products take up more space than the original pure iron. In multiple samples, we see the formation of cracks propagating around oxidation zones. These cracks are points of weakness that might enable a piece of slag to delaminate or simply might serve as additional permeability that would increase the impact of water-driven weathering processes.

The precipitation and dissolution of calcite is a common feature for slag from Standish, NY. The formation of calcite is seen in the white chalky rinds on the ~15 year weathering experiment and the precipitate from the 2 month weathering study. The color change (fig. 12) and chemistry changes serve as examples indicating that chemical weathering has stripped calcite from the slag. The acid attacked the calcite more so than wollastonite or gehlenite because only the CaO content decreased in post-leach samples (fig. 16). Sr and Ba are likely to be associated with Ca due to their similar valence states and would be impacted by the acid-induced loss of calcite.

The morphology of slag is essential to determining the weathering rate and processes. For example, vesicular slag will weather quickly because of its porosity and permeability. St-V showed the largest changes in major element chemistry due to acid leaching. This is due to the vesicles throughout the entire sample. St-VA didn't float which means that the sample is both porous and permeable-allowing for a larger surface area for the nitric acid reactions. Vesicular slags also lack glass crusts. When present, glass will slow down weathering processes. This protection will persist until the glass is completely removed through erosion. We suspect that 3 of our slags (St-B, St-NG, and St-GC) represent samples in varying states of weathering due to differing amounts of protective glass. Their trace element chemistry supports the relationship and their morphological differences are merely due to glass loss. The impact of glass-removing weathering is observed in the field where the ground is profusely littered with small pieces of glassy rind that have separated from their crystalline host.

Overall, the change in major oxides when comparing initial slags to their acid leached partners never exceeded 5 wt%. The leaching test was formulated to show extreme acid settings, suggesting that a natural setting might be less impacted. HNO_3 is abundant in acid rain but other acids present in nature might play a more important role in the weathering process.

Conclusion

The slag pile in Standish covers ~12.8 acres of land and sits along a waterway. Slag at the site is clearly weathering physically and chemically, impacting the environment. The slag neutralizes the acidity in the rain of the region, but according to our leaching results, elements are lost which may be troublesome. For example, Frank et al. (1996) found that the use of slag as a fertilizer helped crops grow, but also poisoned cattle eating grass from the fields that were enriched in V and CaO--elements that also are present at Standish. Due to the large size of the slag pile it will have a long term impact on the surrounding environment of Standish, NY.

References

Dawson, J.C., Moravek, J.R., Glenn, M.F., and Pollard, G.C., 1988, Iron Industry of The Eastern Adirondack Region,Field Trip Guidebook: Plattsburgh, New York, New York State Geological Association (NYSGA), p. 166–168.
Driscoll, C.T., Driscoll, K.M., Mitchell, M.J., and Raynal, D.J., 2002, Effects of acidic deposition on forest and aquatic ecosystems in New York State: Environmental Pollution, v. 123, p. 327–336, doi: 10.1016/s0269-7491(03)00019-8.
Farthing, D.J., Sidlauskas, S., 2007, Slag From Standish, NY- A Boon or A Bane?: Geological Society of America Poster
Frank, A., Madej, A., Galgan, V., and Petersson, L., 1996, Vanadium poisoning of cattle with basic slag. Concentrations in tissues from poisoned animals and from a reference, slaughter-house material: Science of The Total Environment, v. 181, p. 73–92, doi: 10.1016/0048-9697(95)04962-2.
Keller, A.T., 1932, Hagley Digital Archives:
https://digital.hagley.org/islandora/search?type=dismax&f%5B0%5D=mods_relatedItem_host_location_shelfLocator_ms%3ASeries%5C%20II%2C%5C%20Box%5C%2019%2C%5C%20Folder%5C%20106A (accessed March 2019)
Tolonen, E., Sarpola, A., Hu, T., Rämö, J., and Lassi, U., 2014, Acid mine drainage treatment using by-products from quicklime manufacturing as neutralization chemicals: Chemosphere, v. 117, p. 419–424, doi: 10.1016/j.chemosphere.2014.07.090.
Aerial photo: 2017 12-inch Resolution 4-Band OrthoimageryEast Zone (2017) [downloaded file]. NYS Office of Information Technology Services, GIS Program Office, Albany, NY. URL: https://orthos.dhses.ny.gov/# [May, 2019]
DEM: USDA 1 Meter DEM (2016) [downloaded file]. NYS Office of Information Technology Services, GIS Program Office, Albany, NY. https://orthos.dhses.ny.gov [Sept.,2019]

Acknowledgements: We would like to thank Dr. Dori Farthing, Dr. Sarah Gaudio, and Miguel Baique for all their support in this study. We would also like to thank Dr. Amy Sheldon for helping us with the filtration of our water samples.