UNIVERSITY OF NORTH DAKOTA

PHASE TWO FINAL REPORT

Project 5

Steven A. Benson, Nicholas Lentz, Shuchita Patwardhan, Junior Nasah, Charles Thumbi and Harry Feilen.

University of North Dakota
Institute for Energy Studies
Upson II Room 366
243 Centennial Drive, Stop 8153
Grand Forks, ND 58202-8153

Srivats Srinivasachar
Envergex, LLC

7/26/2012

Table of Contents

List of Figures

Figure **Page**

List of Tables

Summary

Green balls produced from concentrate/filter cake and additives obtained from five of the taconite facilities operating on the Mesabi Iron Range were combined with trace amounts of ESORB-HG-11. ESORB-HG-11 is a proprietary brominated powdered activated carbon. The green balls containing ESORB-HG-11 were then subjected to heating experiments to determine the mercury oxidation potential of the additive.

Heating tests of the green balls from four of the facilities gave mercury oxidation levels ranging between 43% and 78%, with averages of 52% (±8%) and 58% (±11%) for additive amounts of 0.1weight% and 0.5wt%, respectively. Baseline oxidations averaged 18% (±6%), while oxidation due to ESORB-HG-11 averaged 42% (±9)% and 48% (±13)% for the 0.1wt% and 0.5wt% additive loading respectively. The results confirm preliminary results obtained in Phase 1 of this project, and indicate that the 0.1weight% ESORB-HG-11 loading is optimal for mercury oxidation, and is recommended for any potential future work involving the technology. The results obtained from a fifth facility, United Taconite, were not included in determining the averages, as they showed significantly lower mercury oxidation increases for ESORB-HG-11-containing green balls. The oxidation levels observed were approximately 10% to 15% lower than those observed for the other plants. The possible reason for this difference was not conclusively established during the testing.

The green balls were produced by the Coleraine Minerals Research Laboratory (CMRL) of the Natural Resources Research Institute (NRRI) and were subjected to industry-standard, Batch Balling tests to determine the possible effects the additive might have on the physical properties of the green balls. The physical properties investigated consisted of the moisture content, wet drop number, and dry compressive strength. For the samples with 0.1weight% additive, no significant difference due to addition of ESORB-HG-11 was observed with respect to the baseline standard during the batch balling tests. Slight differences from the baseline standard were observed with the 0.5weight% additive loading, suggesting that the 0.1weight% is the optimal additive loading.

Preliminary tests performed during Phase 1 of this project determined that there was little or no gas-phase mercury oxidation occurring during tests performed using the bench scale apparatus. This suggests that the mercury oxidation observed during these tests is a solid phase phenomenon occurring most likely on the carbon surface and within the green ball. Previous work indicates that gas-phase mercury oxidation does occur in taconite facilities with bromide addition to the green ball which enhances baseline (no bromide addition) mercury oxidation values. Consequently, a full-scale demonstration of the technology might result in higher levels of mercury oxidation than observed during the bench scale tests in this project. No tests were performed in this project to determine the impact of the carbon additive on the fired taconite pellet; this aspect should be investigated in future testing.

Background

Problem

The taconite industry has been identified as one of the major contributors of atmospheric mercury in the Lake Superior basin by the Lake Superior Lakewide Management Plan (LAMP) [Taconite Mercury QAPP]. Mercury is a leading concern among the air toxic metals addressed in the 1990 Clean Air Act Amendments because of its volatility, persistence and bioaccumulation as methylmercury in the environment, and its neurological health impacts.

In order to address this problem, the Minnesota taconite industry set a goal of achieving a 75% reduction in mercury emissions from the industry by the year 2025, with current industry wide emissions estimated at 440 to 880 lb/yr [Berndt 2003]. Several projects were then selected by the Minnesota Taconite Mercury Control Advisory Committee (MTMCAC) to identify the different existing mercury control technologies that show a potential to achieve 75% reduction.

Previous research work done at taconite processing plants by the Minnesota Department of Natural Resources (DNR) identified the ore as the main source of mercury during taconite processing [Berndt 2003]. This ore undergoes a series of beneficiation steps through which it is processed into small spherical balls referred to as green balls. Mercury is released during induration (heat processing) of these green balls to a final product referred to as taconite pellets. Previous work suggests that the release starts at temperatures of approximately 200^{o}C and continues well up to temperatures of 600^{o}C [Galbreath et al 2005], which corresponds to temperatures seen in the pre-heat zone of the induration furnaces.

In order to address this mercury emission problem, an approach was proposed by the University of North Dakota (UND) team in response to a Request for Proposals (RFP) issued by the Minnesota DNR. This approach explores the possibility of oxidizing the mercury before it is released from the green balls.

Green Ball Production

To produce green balls taconite ore undergoes a series of beneficiation steps which can be subdivided into [EPA]:

- Liberation, which involves crushing followed by grinding to release the desired ore from the gangue material.
- Concentration, here magnetism and/or flotation are used to separate the ore from the rest of the gangue material.
- Agglomeration, in which the concentrated ore mixed with water, a binder and certain additives; is ‘tumbled’ in a balling drum or disc to produce green balls.

The final chemistry of the green balls before induration depends on the concentrated ore composition and the additives used in the agglomeration step. Taconite facilities employ different formulations during their respective agglomeration steps. These formulations control the type of binder used, binder/concentrate ratio, moisture content of the pellets, and additives used. The final chemistry of the green balls is considered important with respect to the proposed technology for mercury oxidation within the green balls.

This study focuses on five of the taconite facilities currently operating on the Mesabi Iron Range: United State Steel's Minntac and Keetac; United Taconite (Utac), Arcelor Mittal and Hibbing Taconite (Hibtac). This report details the results obtained when a mercury oxidizing additive – ESORB-HG-11, is combined with green balls from each taconite facility. The green balls/ESORB-HG-11 combination is produced according to the formulations of each respective facility.

Proposed Technology

The proposed technology employs a low-corrosivity carbon based mercury oxidizing agent/additive. The additive is a proprietary enhanced Powdered Activated Carbon (PAC) known as ESORB-HG-11, and is to be added in trace quantities to green balls prior to induration. ESORB-HG-11 is a proven effective catalytic oxidation agent that then acts as a fixed bed catalyst for mercury oxidation. ESORB-HG-11 contains only trace amounts of halogens thus reducing the possible occurrence of halogen driven corrosion.

This report is a follow up to the Phase 1 report that focused on establishing the potential and optimum loading of ESORB-HG-11 to oxidize mercury present in green balls. This report focuses on laboratory scale work performed to establish the extent oxidation achievable when ESORB-HG-11 was included in the formulation of green balls obtained from five taconite facilities. ESORB-HG-11 loadings of 0.1wt% and 0.5wt% were used for the duration of the test, based on optimum loading established during the Phase 1 testing. The main goals of these tests were:

- Establish potential oxidation levels achievable by including ESORB-HG-11 in green ball formulations.
- Perform chemical analyses on test products to better understand mechanism of mercury oxidation.

Green balls used for the testing were prepared by the Coleraine Minerals Research Laboratory (CMRL). Preparation was done according to a batch balling procedure established by CMRL and based on the green ball formulations of each respective facility.

Approach

Green ball Production for Phase 2 Testing

Phase 2 tests employed green ball samples produced by CMRL. The balls were produced following a "Batch Balling" procedure established by CMRL, which used the formulations of each respective plant to produce the green balls. CMRL is an established testing facility for iron ore related bench and pilot scale experiments. Several different tests related to the taconite industry are performed by CMRL including batch balling studies. Their batch balling procedure is known and accepted by the taconite industry.

The CMRL balling procedure involved first obtaining concentrates from each respective facility and performing a moisture test. Minntac provided a filter cake that was received as a slurry and pressure filtered to the facility's required moisture standard. The green ball chemistry and moisture content were adjusted to be representative of each respective taconite facility's standard, as determined necessary. The ESORB-HG-11 was then added to the concentrate batch by sprinkling, followed by hand blending in a mixing bowl. The blending technique has been employed exhaustively as a method of adding small quantities of additives to green ball formulations; it is a proven and reliable combination method. Loading rates used for ESORB-HG-11 in the green balls were 0.1wt% and 0.5wt%.

The binder was added along with ESORB-HG-11 during the sprinkling method. Once blended, small amounts of the new concentrate containing the additive and binder were then introduced into a balling tire, see Figure 1. "Seed" balls of -3 to +4 mesh were then produced, as seen in Figure 2. A specified amount of the "seed" balls (170 to 250g) was used to "grow" the green balls by gradually adding concentrate to the seeds until they reached the target size. The "growing" step took on average 3 minutes, and was followed by a "rolling" step that lasted for a minute. Final green ball sizes were -1/2" +3/8", see Figure 2. A size distribution of the green balls was also determined; this distribution is a relative value and is used as a measure of the green ball growth rate during batch balling.

Once the green balls were formed, they were screened to determine the size distribution. A sample of the green balls prepared, approximately 200-300g, was placed in a drying oven to determine the moisture content; meanwhile another sample of 10 green balls was subjected to an 18" wet drop test. Ten of the dried green balls from the moisture test were then subjected to a dry compressive strength test. The results of the different tests are presented in Appendix B. The remaining green balls were stored in plastic bags and transported back to the University of North Dakota (UND) for oxidation testing.

Green balls were produced for all the facilities. For each facility a batch was prepared containing no additive (baseline), 0.1wt% additive and 0.5wt% additive. A replicate of either the baseline, 0.1wt% or 0.5wt% batch, was also prepared, depending on the facility. This gave a total of four batches per facility except for Hibtac. Hibtac uses two different formulations for their green balls, so two different sets of batches were made for Hibtac, for a total of 8 batches.

Figure 1. Picture of “Balling” tire assembly.

Figure 2. Pictures showing a) green ball “seeds” b) Sieved green balls.

Pellet Testing Equipment

The bench-scale apparatus is illustrated in Figures 3 and 4. It consisted of a tube furnace, reaction vessel, gas metering system, gas conditioning system, mercury pretreatment system, and mercury analyzer. The testing procedure involved placing approximately 100g of green balls into the reaction vessel and heating the green balls up to 700°C. During the heating process, air flow to the vessel was maintained at 7.5 Lpm to ensure the system was under positive air pressure negating any effects of leaks on mercury concentration in sample gas. A portion of the flow leaving the reaction vessel was sampled through heated PFA tubing to a pretreatment system, and then directly to the analyzer for elemental mercury determination. Excess air was vented through a carbon bed. Initial experiments were conducted with an air flow rate of 5 Lpm and a final temperature of 700°C before modifications were made to the test system including an increase in the air flow rate to ensure constant positive air pressure in the system.

Before each run, the Horiba mercury analyzer was either calibrated or its calibration verified. While the analyzer was calibrated, the PFA tubing and other parts that would contact reactor outlet gases were preheated to 150°C to prevent condensation or reduction of oxidized mercury in the lines during the experiment. The furnace reactor was also preheated to 700°C and then allowed to cool to 250°C to drive out any residual mercury in the furnace. During testing, once the green balls were added to the reactor the temperature of the reactor was increased to 700°C at a ramp rate of 20°C/min based on full-scale conditions. Note that due to heat losses in the bench scale assembly, the actual ramp rate decreased as the temperature of the reactor bed increased, resulting in a slower overall ramp rate when compared with full-scale conditions.

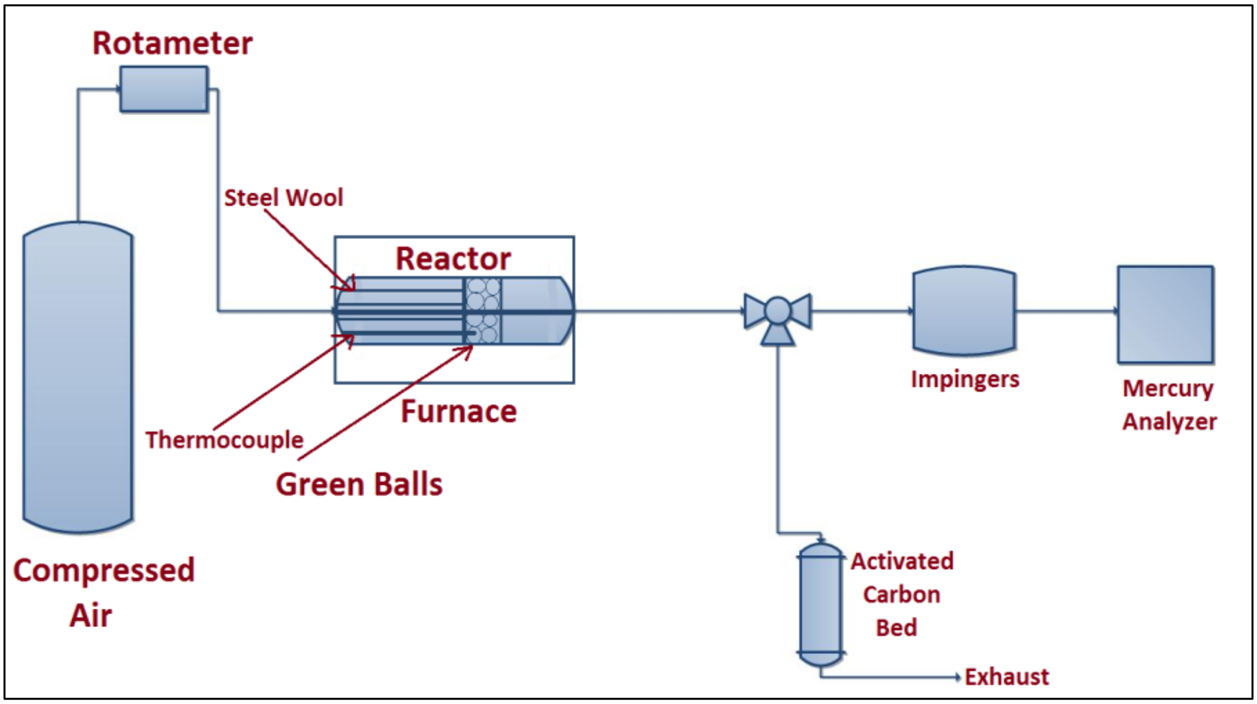

Figure 3. Schematic of testing equipment.

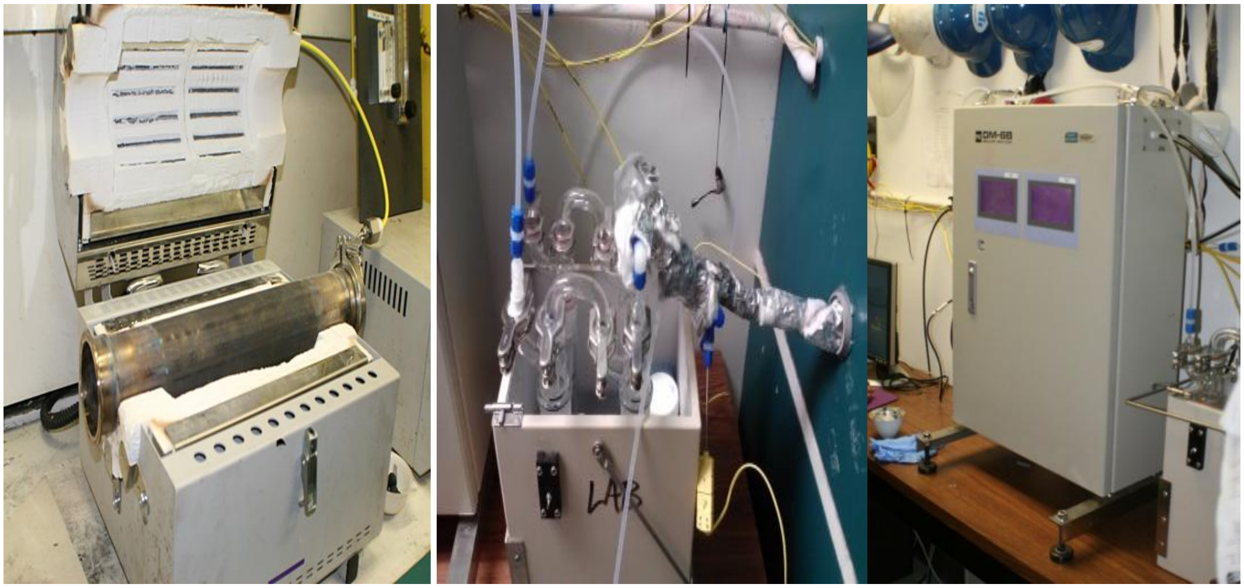

Figure 4. Pictures showing reactor vessel, Wet-chemistry impinger train, Horiba DM-6B mercury analyzer.

A wet chemistry pre-treatment system was used to condition the sample gases before mercury analysis. It consisted of two parallel sets of impingers: one for determining Hg^0 concentration in sample gas, while the other for determining Hg^T concentration in the sample gas. The set-up was designed based on a modified wet chemistry PS Analytical pre-treatment conversion system and ASTM D6784-02 (also known as the Ontario Hydro [OH] method). In this design, the first impinger train is for conditioning the elemental mercury stream. It consists of two impingers in series sitting in an ice bath. The first impinger contains a 150 mL of 10% w/v potassium chloride (KCl) and 0.8% w/v $Na_2S_2O_3$ solution that captures the oxidized mercury in order to obtain only elemental mercury concentration, while the second impinger traps all moisture present in the gas sample before analysis by the mercury analyzer. The second impinger train is for conditioning the total mercury stream. Here, the first impinger contains 150 mL of 0.8% w/v stannous chloride ($SnCl_2$) solution and 20% w/v of NaOH. The $SnCl_2$ reduces the oxidized mercury in order to obtain a total mercury measurement of the flue gas. This impinger train also sits in an ice bath. The second impinger traps all moisture present in the gas sample before analysis. The trains were modified from a continuous flow to a batch system.

The Horiba mercury analyzer simultaneously and continuously measures both total and elemental mercury. The difference between the total and elemental is taken as oxidized mercury. The mercury measurements are plotted on an XY curve at an interval of 10 seconds per measurement. The mercury measured can then be estimated by calculating the area under the curve for both Hg^0 and Hg^T. With the calculated values, the percent oxidation and mercury concentration of the green balls can be estimated. Gas flow rates are measured with rotameters and were validated with mass flow controllers.

Test Matrix

Table 1 summarizes the test matrix for Phase 2 testing. All batches prepared by CMRL were tested in triplicates except for replicate batches which were tested in duplicates. During test runs, the total mercury concentration [Hg^T] and elemental mercury concentration [Hg^0] were measured and used to estimate the percent mercury oxidation, which was assumed to be an estimate of the removal potential if there was a wet scrubber present downstream of the test equipment. The equation for estimating percent mercury oxidation/removal is discussed in the *Data Quality Assessment* section and in Appendix C.

Table 1. Summary of Phase 2 Runs.

Facility	Pellet Type	Loading (wt.%)	Number of Runs
Minntac	Flux	Baseline	2
		Baseline Replicate	2
		0.1	3
		0.5	3
Keetac	Flux (low level limestone)	Baseline	3
		0.1	2
		0.1 Replicate	2
		0.5	3
Arcelor Mittal	Standard	Baseline	3
		0.1	2
		0.1 Replicate	2
		0.5	3
Utac	Standard	Baseline	3
		0.1	3
		0.5	2
		0.5 Replicate	2
Hibtac	Standard	Baseline	3
		0.1	3
		0.5	2
		0.5 Replicate	2
	High Compression	Baseline	2
		Baseline Replicate	2
		0.1	3
		0.5	3

Analytical Methods

To obtain insight on the mechanism governing mercury oxidation i.e. surface chemistry of green balls during oxidation, a series of analytical tests were carried out. The tests consisted of Mössbauer spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis-differential scanning calorimetry (TGA-DSC). The tests sought to investigate the changes occurring as the green balls were heated, and determine possible effect the changes had on mercury release. Results from these analyses are discussed later in this report.

Results and Discussion

The results obtained during Phase 2 testing are sub-divided into 5 sections, each section representing the results from each taconite facility. Some graphs are included in this section for illustration purposes while the rest of the graphs can be found in appendix A. A total of ten runs were done for each type of pellet produced by the facilities.

Batch balling tests were also conducted on the green balls produced to compare the physical quality of the green balls prepared with the additives. No significant differences were observed during the tests between the 0.1wt% loading and the baseline standard used for comparison. However, for the 0.5wt%, a few differences were observed such as the size distributions which were slightly larger (+1/2” size fraction) than the baseline. The size distribution is a measure of the green ball growth rate, meaning that the green balls apparently “grew” faster when containing more additive as compared to the additive-free green balls. The next difference observed was the dry compression test results for Hibbing Taconite standard green balls and Keewatin Taconite green balls which were lower for the high additive load rate. The data used was not sufficient to conclusively determine that these differences were significant. The full report is presented in Appendix B.

The Batch Balling Test results suggest that the 0.1wt% is the optimal loading for testing as no significant difference between additive green balls and baseline green balls was observed during these tests. More tests are however recommended to investigate if there is any effect of the additive on the quality of fired green balls (taconite pellet).

Data Quality Assessment

A key objective of the bench tests was to provide a possible estimate of the potential reduction capability of the technology if deployed at an actual taconite facility. To estimate this reduction potential, the average oxidation due to addition of ESORB-HG-11 only was estimated. This required assumption that all oxidized mercury released from the taconite processes would get captured by the scrubber system and that any mercury re-emission from the scrubber waters is negligible. The equation used to determine reduction potential was:

$$\text{Reduction Potential} = \frac{\text{Hg}[2]-\text{Hg}[1]}{100-\text{Hg}[1]} * 100 \quad [1]$$

Where,

- Hg[1] is the average mercury oxidation for baseline runs for respective facility, expressed as a percentage.
- Hg[2] is the average mercury oxidation for 0.1wt% ESORG-HG-11 runs for respective facility, expressed as a percentage.

Certain factors are not accounted for when using the bench scale results to estimate potential mercury oxidation. The first is gas phase oxidation. Phase 1 testing established that little or no oxidation was observed when bromine salts were added to carbon-free green balls. This suggested that there was little or no gas phase oxidation during bench tests. However, gas phase oxidation is considered to occur during field tests [Berndt, Engesser 2005]. Consequently, it is very possible that the reduction potential observed during bench tests would be lower than those observed during potential full-scale testing.

Secondly, the goal of increasing the ratio of oxidized mercury to total mercury is to increase the amount of mercury that could get captured in the wet scrubbers. This approach would prove successful only for facilities that discharge their scrubber solids and/or liquids, providing an "exit" for the mercury captured by the system. Recycling of both scrubber solids and liquids re-introduces the captured mercury back into the process, negating the benefits of using the technology. The results obtained for each facility are presented below.

Minntac Test Results

Table 2 presents the results for all Minntac tests performed and Figures 5 and 6 show the release profile for the baseline and 0.1wt% run respectively. The baseline batch obtained from CMRL was replicated, so duplicate runs of each baseline batch were performed. Both baseline batches showed very good agreement with average oxidation values of 25.7% and 22.3%. Good agreement of the results confirms the reliability of the "Batch Balling" production technique.

Results for ESORB-HG-11-containing batches, 0.1wt% and 0.5wt%, showed very close agreement with mercury oxidation averages of 61.6% and 62.9% respectively. With a baseline oxidation average of 24%, the ESORB-HG-11 reduction potential was estimated to be 49.4% and 51.2% for the 0.1wt% and 0.5wt% loading respectively. The small relative difference between results of both loadings confirms the results obtained during the Phase 1 tests that suggested 0.1wt% to be the optimum loading of ESORB-HG-11 in green balls. All the additive runs showed oxidation levels greater than 50%.

To better understand the effect of temperature on the mercury release profile for Minntac, plots of the percentage of mercury evolved (elemental and total) against the pellet core temperature were made in Figures 7 and 8. The release profiles for duplicate/triplicate runs during Minntac testing were consistent. Consequently, percentage mercury evolved of one run from a particular loading, say 0.1wt%, is representative of the other loadings. Figures 7 and 8 show curves of three runs: baseline, 0.1wt% and 0.5wt%. The percentage of Hg^0 and Hg^T evolved was plotted against the temperature of the pellet core. This plot generated a curve that shows the "rate" at which mercury is evolved as a function of temperature.

Table 2. Results for Minntac Green Ball Testing.

Green Ball	Additive	Additive Loading (wt.%)	Observed Oxidation Test Runs (%)	Average	Reduction Potential (%)	Average
Minntac	ESORB-HG-11	Baseline Replicate	17.3 27.4	22.3	N/A	N/A
Minntac	ESORB-HG-11	Baseline	26.8 24.7	25.7	N/A	N/A
Minntac	ESORB-HG-11	0.1	64.2 53.5 67.1	61.6	52.9 38.8 56.7	49.4
Minntac	ESORB-HG-11	0.5	68.0 61.2 59.6	62.9	57.9 48.9 46.8	51.2

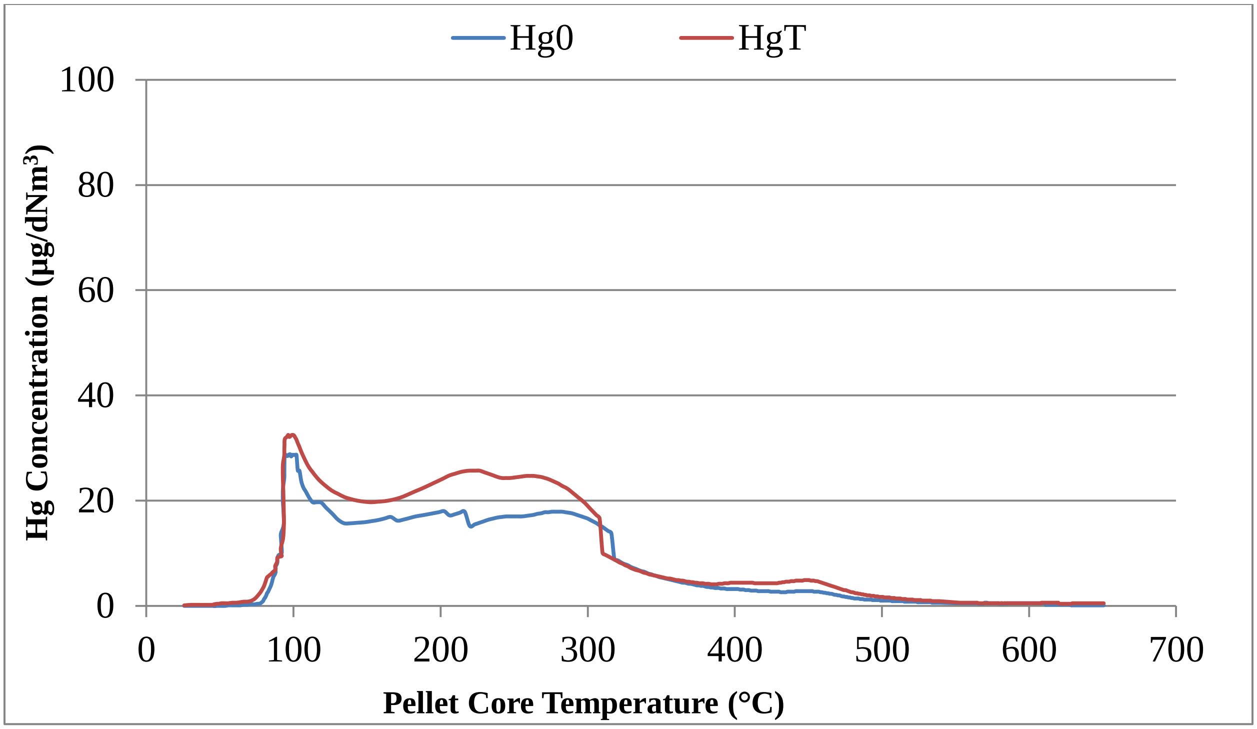

Figure 5. Mercury release profile for a Minntac baseline run.

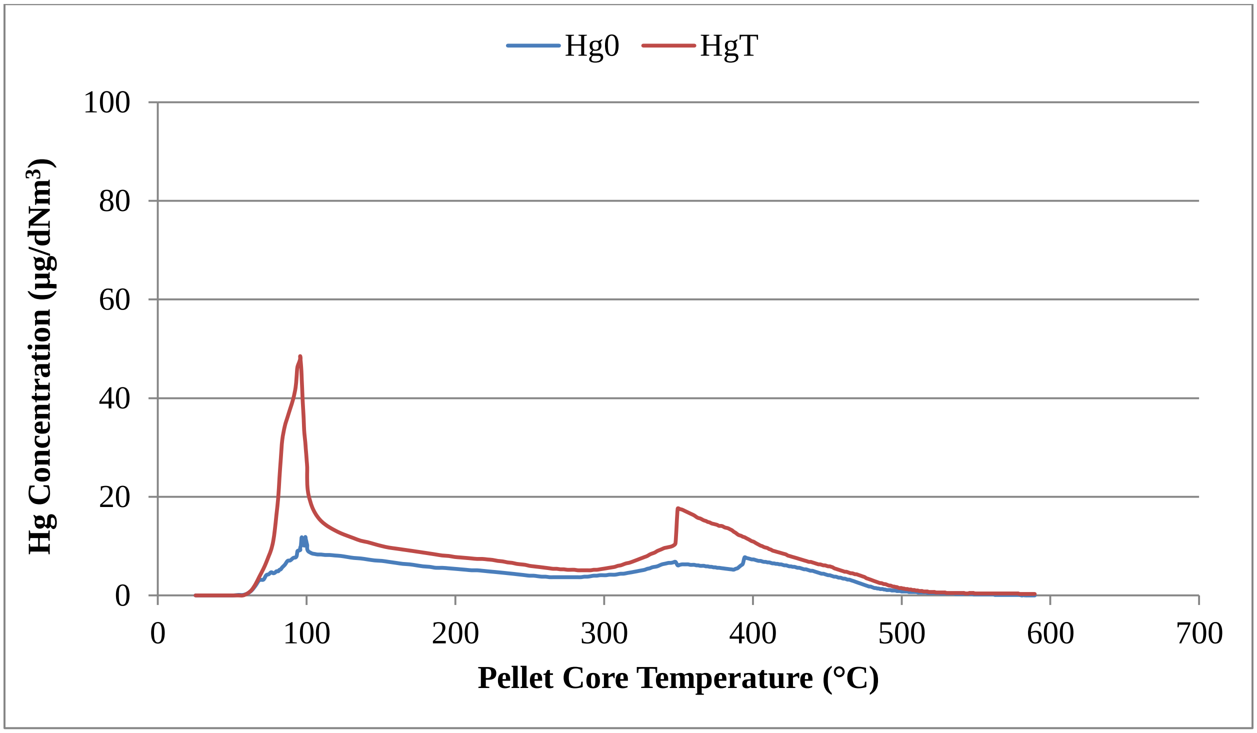

Figure 6. Mercury release profile for a Minntac 0.1wt% loading run.

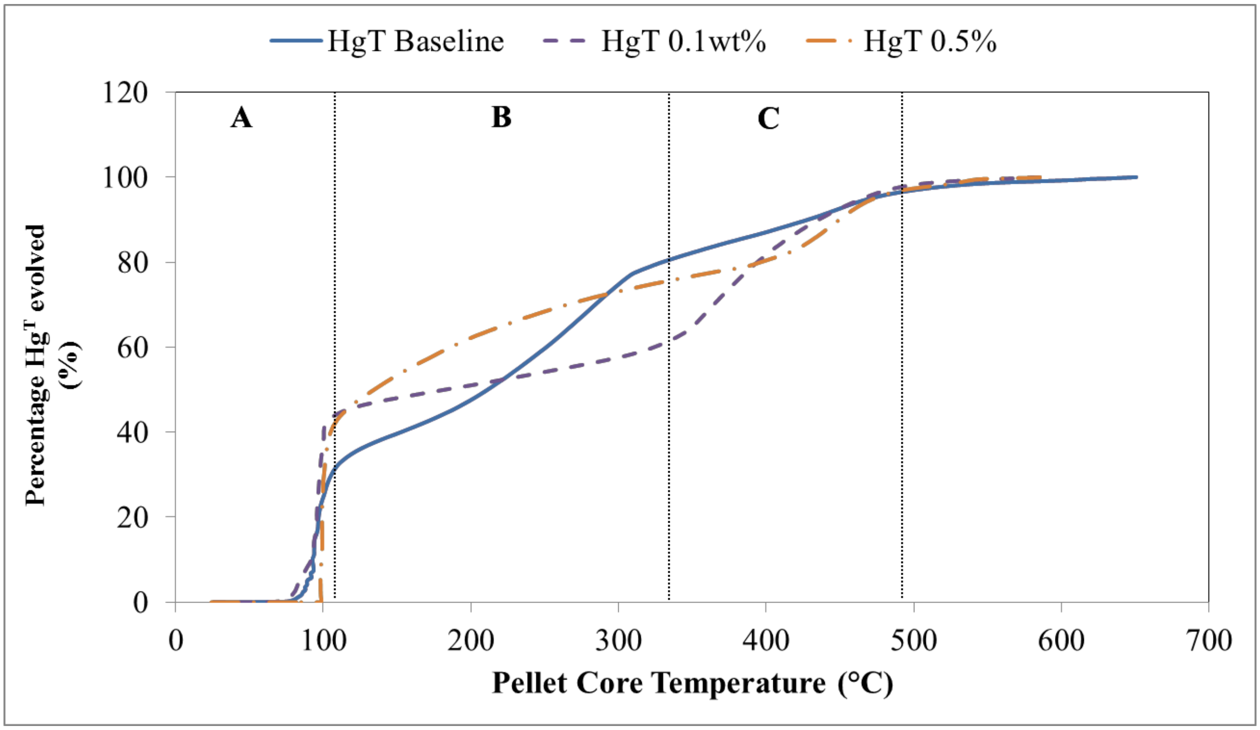

Figure 7. Minntac total mercury (Hg^T) percentage release profile for baseline, 0.1wt% and 0.5wt%; as a function of temperature.

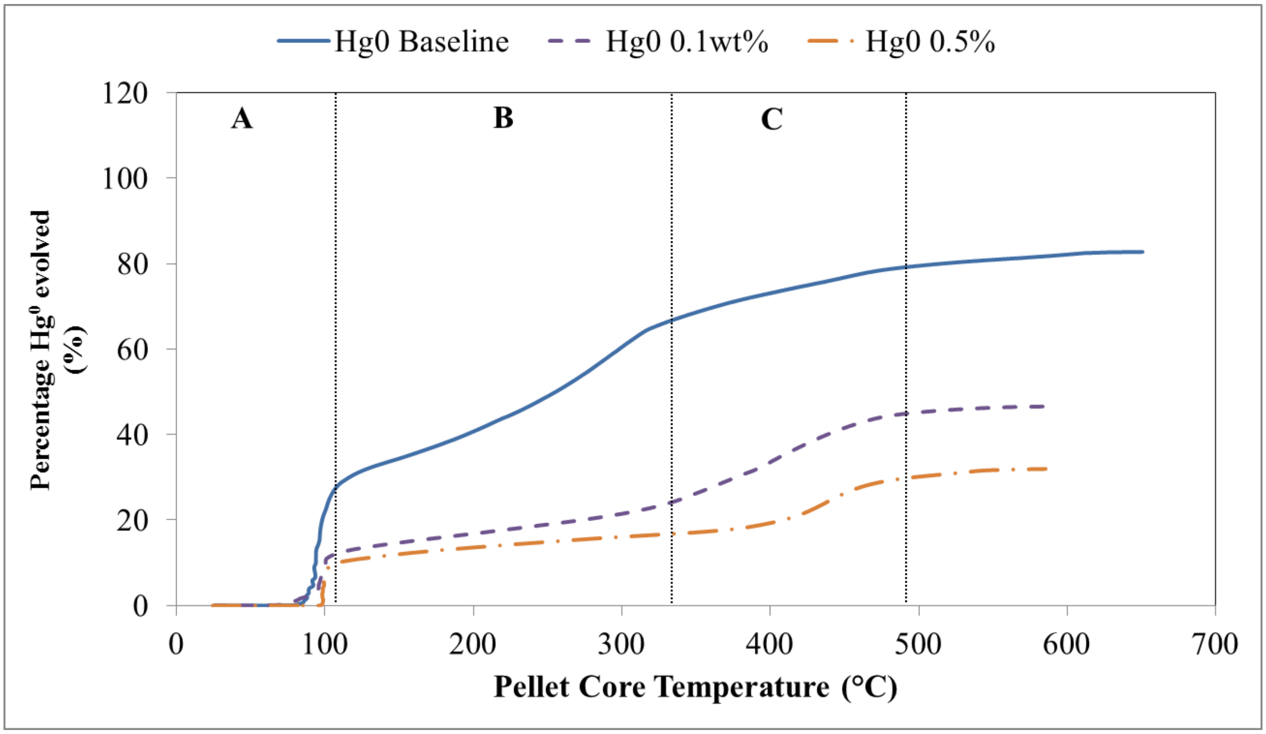

Figure 8. Minntac elemental mercury (Hg^0) percentage release profile for Baseline, 0.1wt% and 0.5wt%.

The percentage plots are divided into three regions: A, B and C. Region A corresponds to the start of heating. In this region the green balls are inserted into the furnace pre-heated to 250°C. The furnace is pre-heated to ensure that the feed air is approximately at 200°C before contacting the inserted green balls. 3 to 5 minutes after the green balls are inserted, a significant mercury release is observed, see Figures 5 to 8. This mercury released is considered to be mercury associated with the surface of the pellets. Recall that the furnace is pre-heated to 250°C, and using a ramp rate of 20°C/min, the temperature of the surface of the green balls during this release is believed to be at least 300°C. In Figures 7 and 8, the release is represented by the steep slope of the curves in region A.

In Figure 7, the percentage of Hg released in region A was higher for both the 0.1wt% and 0.5wt% when compared to the baseline. This seemed to suggest that more mercury was released at the start of the experiment for ESORB-HG-11-containing green balls; however, analysis of the percentage mercury release profiles before pellet core temperatures reached 200°C, for all the runs determined that this behavior was not consistent. So no immediate conclusion was drawn from it.

In region B, the curves appear to "flatten" suggesting that most of the mercury associated with the surface of the pellets has been released. The "flatter" profile suggests mercury release is now occurring from deeper within the pellet as it gradually heats up. Closer observation of the individual curves show that baseline curves are steeper in region B than for 0.1wt%/0.5wt% curves. In region C, the trend is reversed – baseline curves are "flatter" than the 0.1wt%/0.5wt% curves. This phenomenon is possibly due to the oxidation effects of ESORB-HG-11. The mechanism of mercury oxidation by ESORB-HG-11 is believed to consist of a "capture" step, where the mercury is bound to the surface of the carbon; followed by an oxidation step, where the "captured" mercury is then oxidized by the bromine atoms present at the active sites. Therefore in region B, capture of mercury by the carbon slows the rate of mercury release; meanwhile in the baseline curve the absence of carbon does not hinder the mercury release. In region C, the pellet temperature is approximately 350°C, a temperature at which the carbon can probably no longer hold on to the mercury. So all captured mercury is then released from the carbon, as seen for the 0.1wt%/0.5wt% curves, and the carbon no longer exhibits any oxidation capacity as seen in Figures 5 and 6 where no oxidation occurs after 400°C.

This trend is consistent with the other Minntac runs. Graphs displaying the trends are found in Appendix A. The Minntac runs show oxidation of mercury released from green balls during heating tests, with percent oxidations observed as high as 68%. The percentage mercury release curves also give a possible insight into the oxidation mechanism and its dependence on temperature.

Utac Test Results

Table 3 summarizes the results obtained for testing with Utac green balls. 10 runs were performed for Utac testing; however, the results of one run were discarded due to a problem identified with the test equipment during quality control measures. The issue was resolved before testing proceeded. Each batch obtained for Utac testing was tested in triplicates or duplicates and showed good agreement. The average oxidation observed for baseline runs was 21.7%; meanwhile 0.1wt%, 0.5wt% and 0.5wt% replicate runs showed average oxidation levels of 36.8, 34.2 and 37.1% respectively. The reduction potential of the additive only was calculated to be 16.3%, 16.0% and 19.8% for 0.1wt%, 0.5wt% and 0.5wt% replicate respectively. Oxidation for additive-containing green balls ranged from 34% to 37%, approximately 15% decrease from oxidation observed in other facilities. Figures 9, 10 and 11 better illustrate the lower oxidation observed. The possible reason for the lower oxidation observed with Utac samples were not established during testing.

A percentage release plot for Utac data was not included. There was less similarity between release profiles for duplicate/triplicate runs of specific loadings. Consequently, percentage plots for one run of a particular loading are not be representative of the other runs. This makes comparison of runs of different loadings not possible.

Table 3. Oxidation Results for Utac Green Ball Testing.

Green Ball	Additive	Additive Loading (wt.%)	Observed Oxidation		Reduction Potential	
			Test Runs (%)	Average	(%)	Average
Utac	ESORB-HG-11	Baseline	25.7 19.7 19.6	21.7	N/A	N/A
Utac	ESORB-HG-11	0.1	32.9 40.7	36.8	14.3 24.3	19.3
Utac	ESORB-HG-11	0.5	33.9 34.5	34.2	15.6 16.4	16.0
Utac	ESORB-HG-11	0.5 Replicate	28.1 46.2	37.1	8.2 31.3	19.8

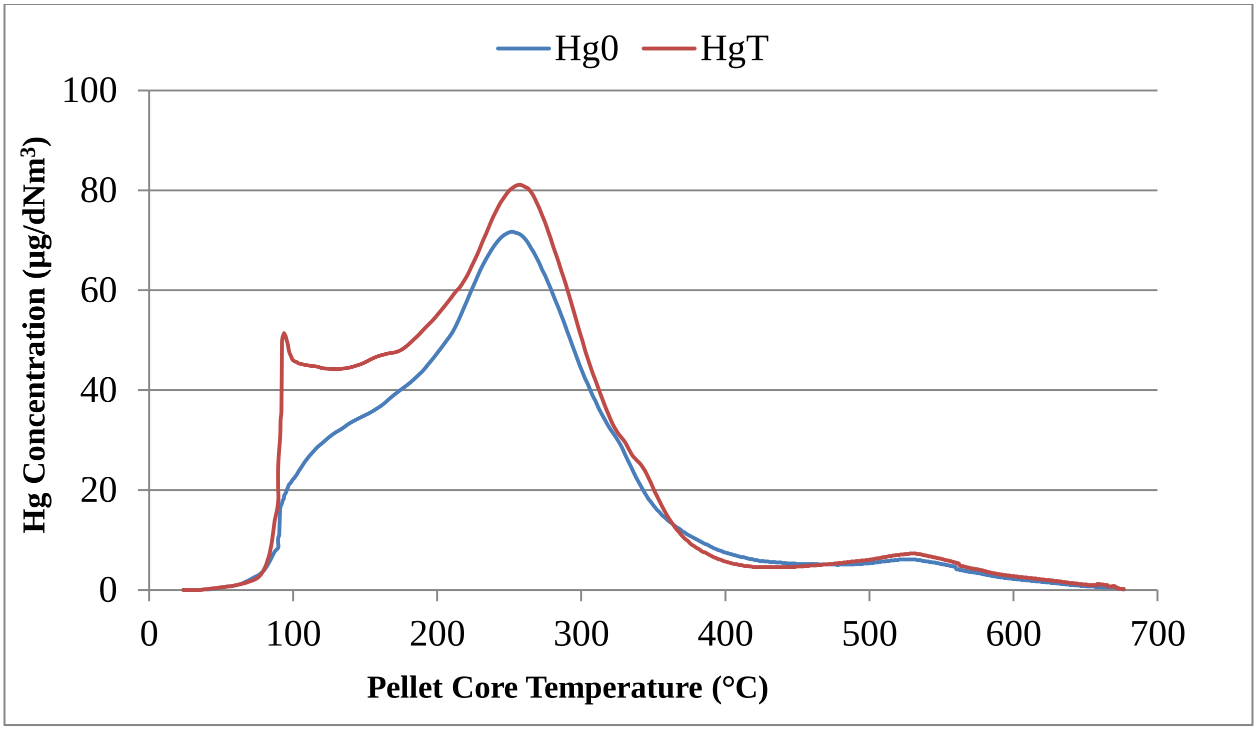

Figure 9. Mercury release profile for Utac baseline run.

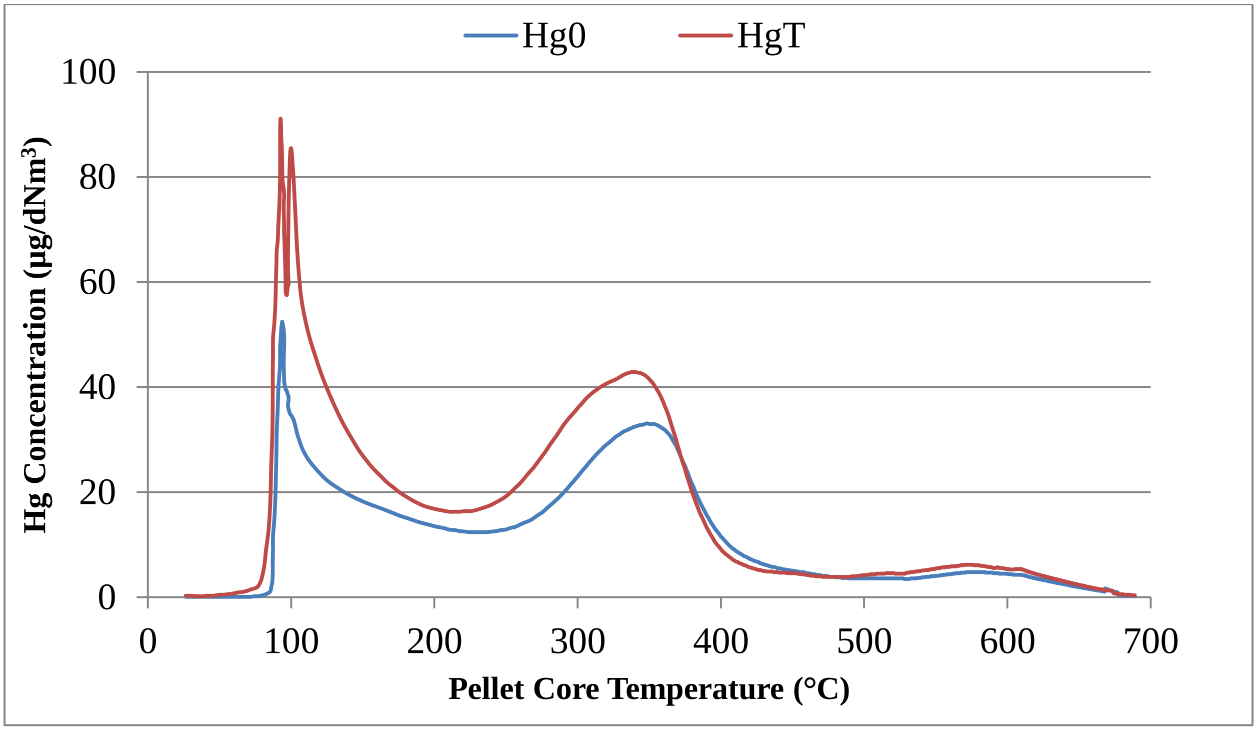

Figure 10. Mercury release profile for Utac 0.1wt% run.

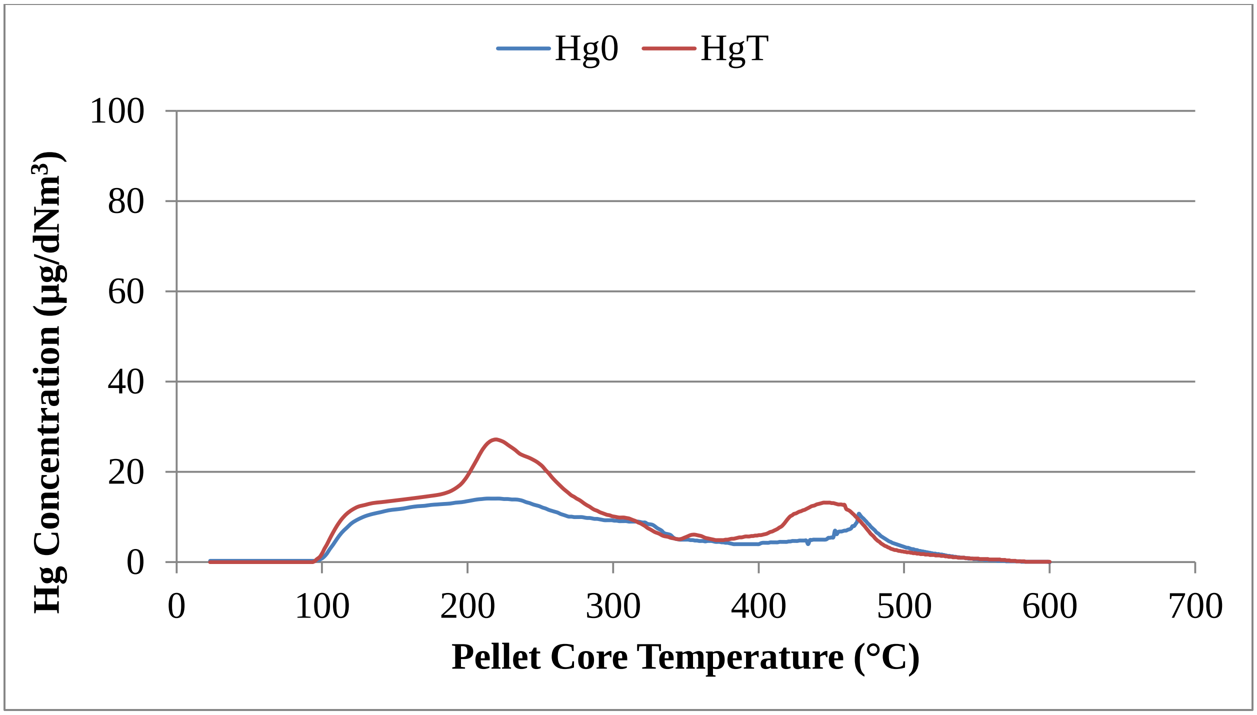

Figure 11. Mercury release profile for Utac 0.5wt% run.

Arcelor Mittal Test Results

The results for Arcelor Mittal are presented in Table 4 and Figures 12 to 15. The average baseline oxidation was 19.9% and showed very good agreement between runs. There were two 0.1wt% green ball batches; each batch gave an average oxidation of 56.9% and 48.2%, with ESORB-HG-11 reduction potential estimated to be 46.2% and 35.4% respectively. The 0.5wt% runs gave an average of 53.3%, with the reduction potential of ESORB-HG-11 only of 41.7%. Looking at the ESORB-HG-11 oxidation only, the difference between the 0.1wt% loading and the 0.5wt% loading was not significant as expected.

Arcelor Mittal runs have similar release profiles for respective loadings as was the case with Minntac. The percentage release plots in Figures 14 and 15 also show curves consistent with those of Minntac. Region C of the plots shows that the increase in the slope for 0.1wt% and 0.5wt% occurs between 400°C and 500°C. Meanwhile in Region A, the amount of mercury released at the start of the run was higher for the carbon runs than the baseline run. Looking at the release profiles for these runs (Figures 12, 13, 40 to 47), for the additive runs, more release and oxidation occurs at the start of the run. Runs were performed randomly and on different test days, so a possible cause of this was not fully determined.

Table 4. Oxidation Results for Arcelor Mittal Green Ball Testing.

Green Ball	Additive	Additive Loading (wt.%)	Observed Oxidation Test Runs (%)	Observed Oxidation Average	Reduction Potential (%)	Reduction Potential Average
Arcelor Mittal	ESORB-HG-11	Baseline	20.0 20.8 18.8	21.7	N/A	N/A
Arcelor Mittal	ESORB-HG-11	0.1	66.4 47.4	56.9	58.1 34.4	46.2
Arcelor Mittal	ESORB-HG-11	0.1 Replicate	53.4 43.0	48.2	41.8 28.9	35.4
Arcelor Mittal	ESORB-HG-11	0.5	49.9 60.1 49.9	53.3	37.5 50.1 37.5	41.7

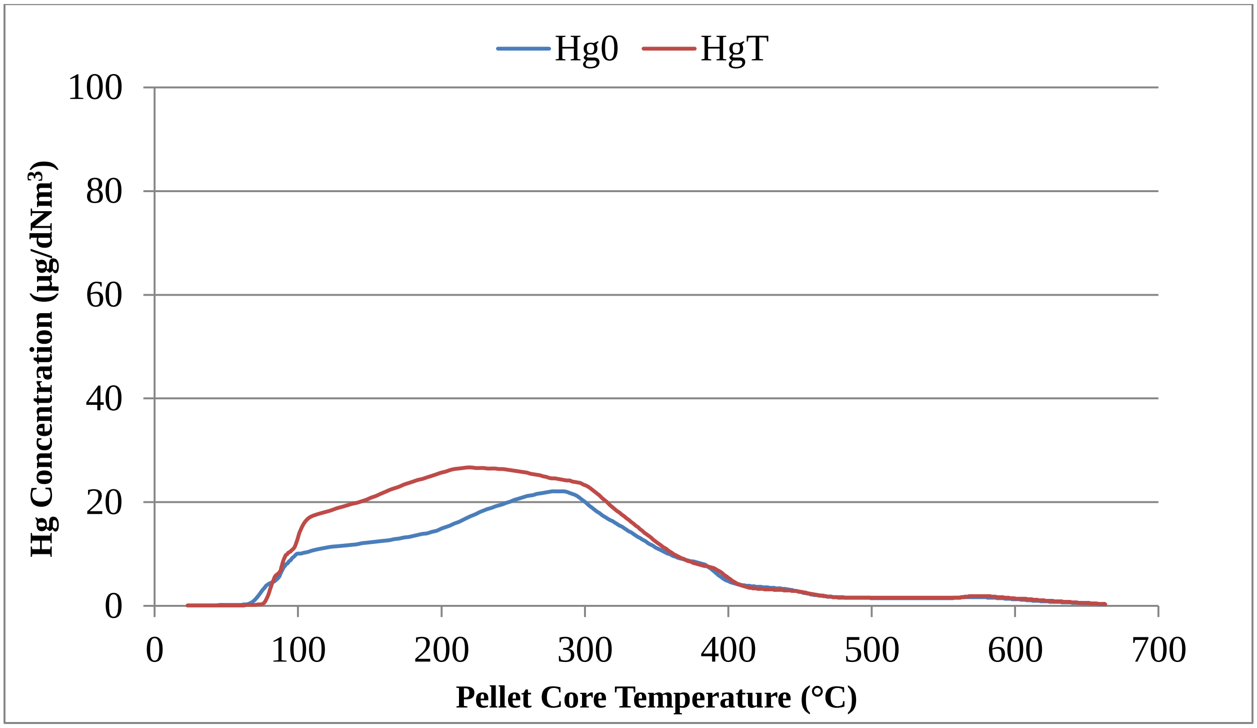

Figure 12. Mercury release profile for Arcelor Mittal baseline run.

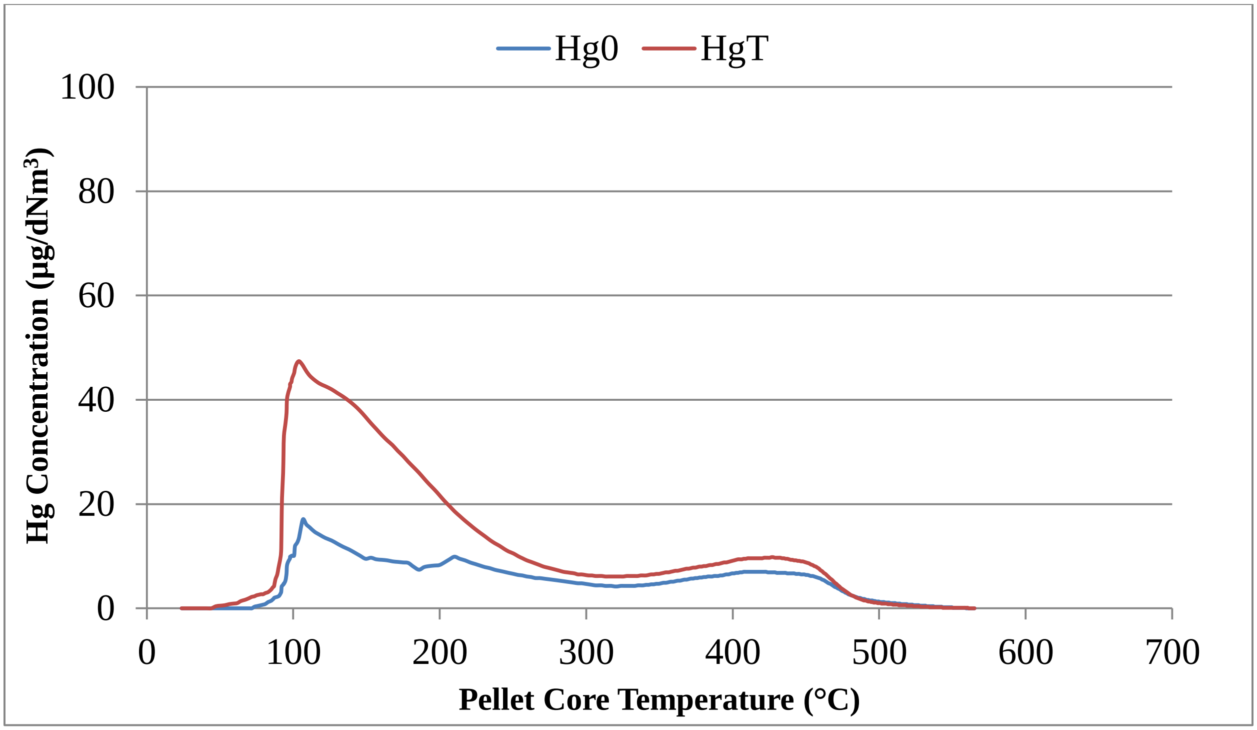

Figure 13. Mercury release profile for Arcelor Mittal 0.1wt% run.

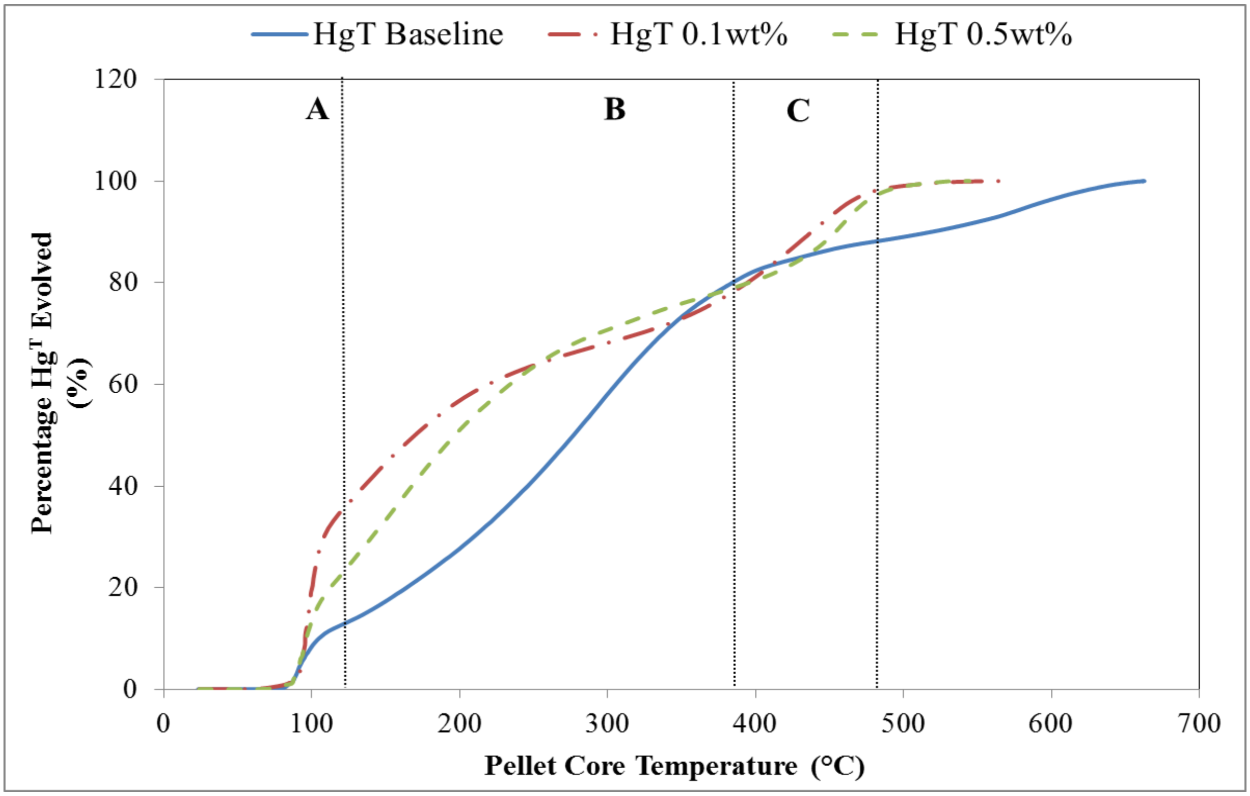

Figure 14. Arcelor Mittal total mercury (Hg^T) percentage release profile for baseline, 0.1wt% and 0.5wt%; as a function of temperature.

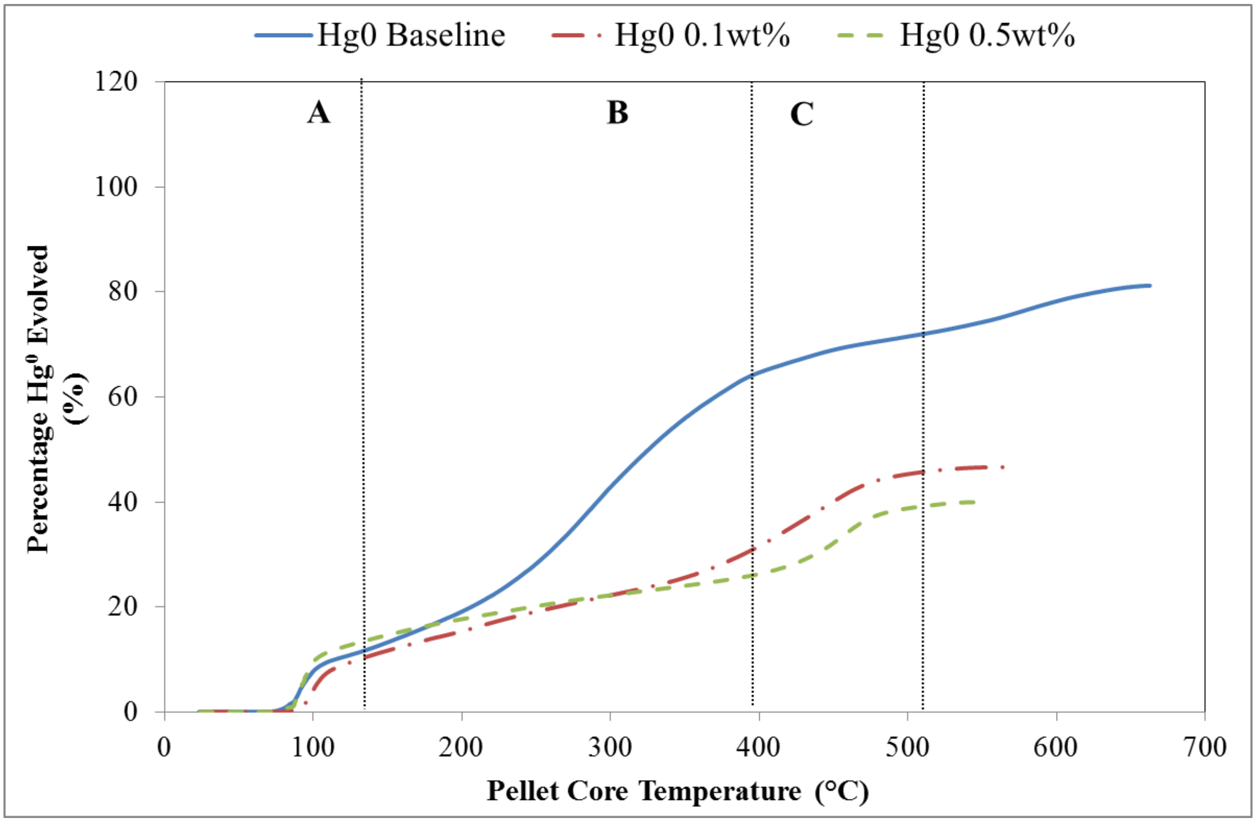

Figure 15. Utac elemental mercury (Hg^0) percentage release profile for Baseline, 0.1wt% and 0.5wt%.

Keetac Test Results

The result's averages are summarized in Table 5. Baseline runs showed good agreement for mercury oxidation with an average of 15.1%. Keetac baseline average mercury oxidation was lower that for Minntac, Utac and Arcelor Mittal. The 0.1wt% batch was replicated and all runs showed very good agreement with an average oxidation of 45.8%. 0.5wt% loading showed slightly higher mercury oxidation with an average of 52.3%. The 0.1wt% and 0.5wt% loadings showed ESORB-HG-11 reduction potential of 38.6% and 43.9% respectively.

Figures 16 to 18 show release profiles for baseline, 0.1wt% and 0.5wt%. A percentage release analysis of Keetac data was not performed because like Utac, there is less similarity between release profiles for duplicate/triplicate runs of particular loadings. Consequently, percentage plots of a particular loading are not consistent.

Keetac results show oxidation results close to values observed for Minntac and Arcelor Mittal confirming further that the additive is also as effective for mercury oxidation for Keetac green balls.

Table 5. Results for Keetac Green Ball Testing.

Green Ball	Additive	Additive Loading	Observed Oxidation		Reduction Potential	
		(wt.%)	Test Runs (%)	Average	(%)	Average
Keetac	ESORB-HG-11	Baseline	-00.4* 16.9 13.3	21.7	N/A	N/A
Keetac	ESORB-HG-11	0.1	43.6 43.8	43.7	33.6 33.8	33.7
Keetac	ESORB-HG-11	0.1 Replicate	44.2 51.5	47.8	34.3 42.9	38.6
Keetac	ESORB-HG-11	0.5	51.5 46.5 59.0	52.3	42.9 37.0 51.7	43.9

* Run not included in average calculation.

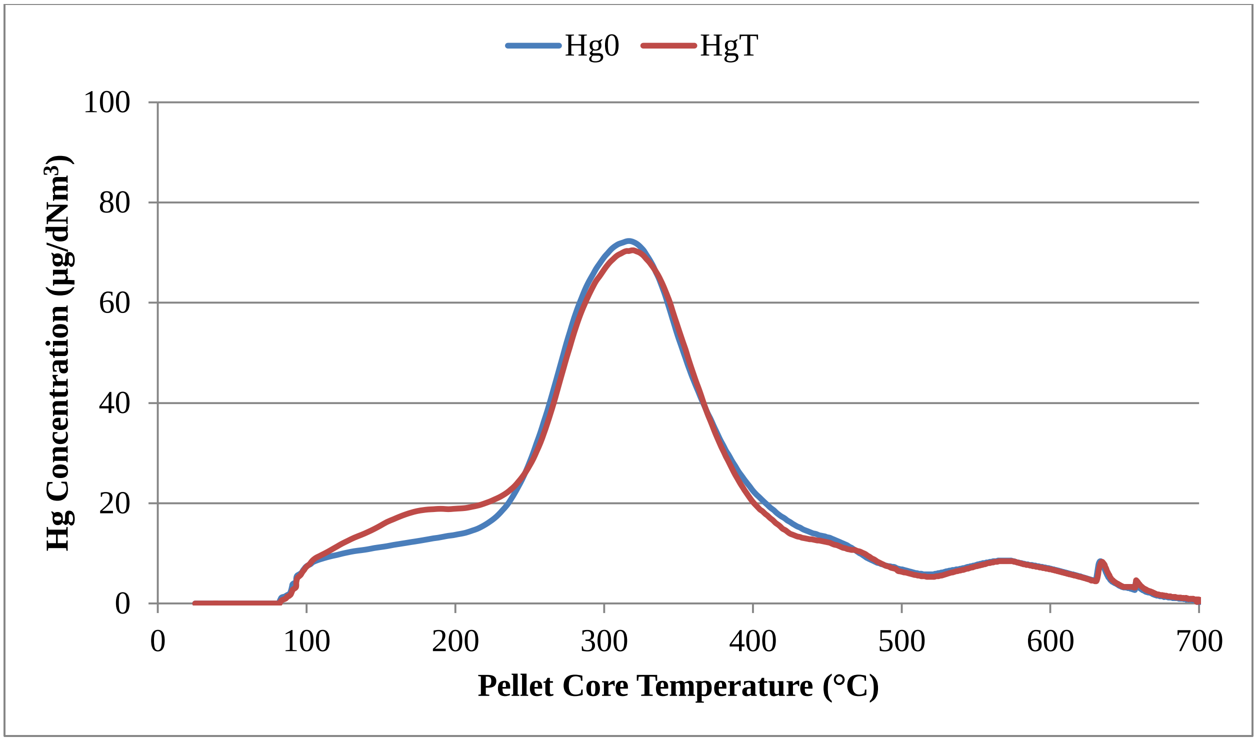

Figure 16. Mercury release profile for Keetac baseline run.

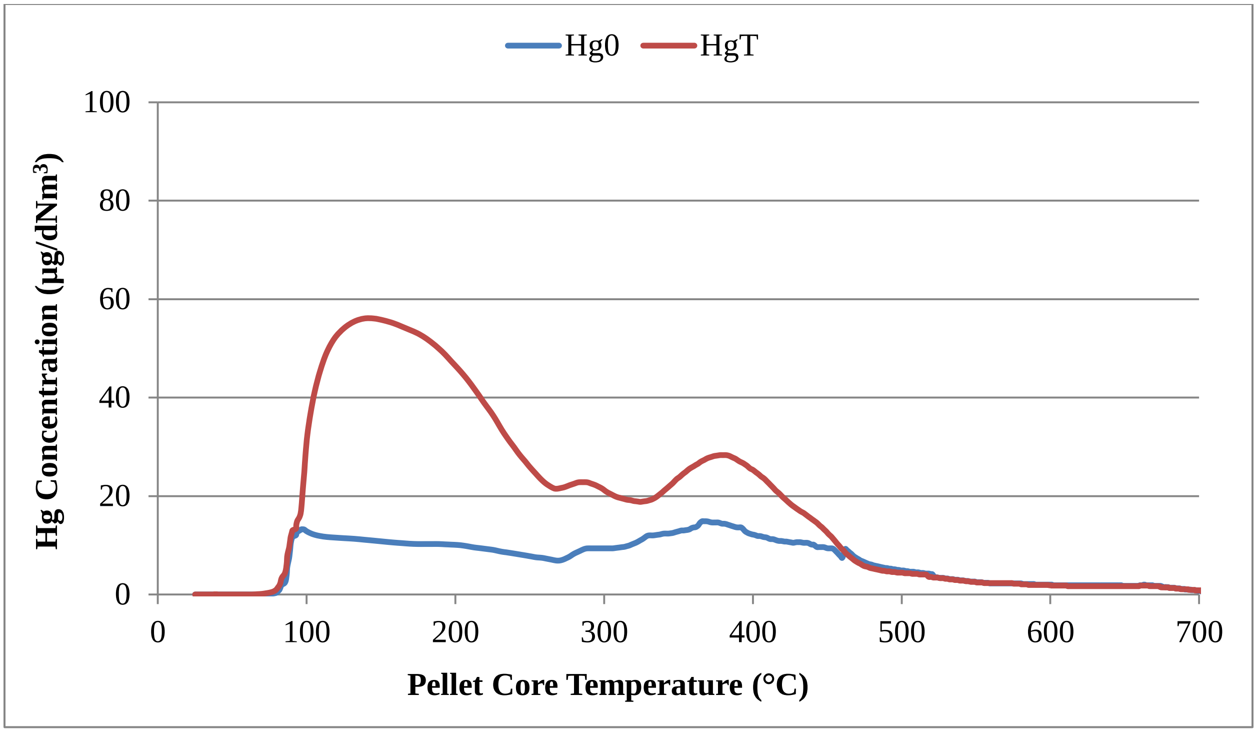

Figure 17. Mercury release profile for Keetac 0.1wt% run.

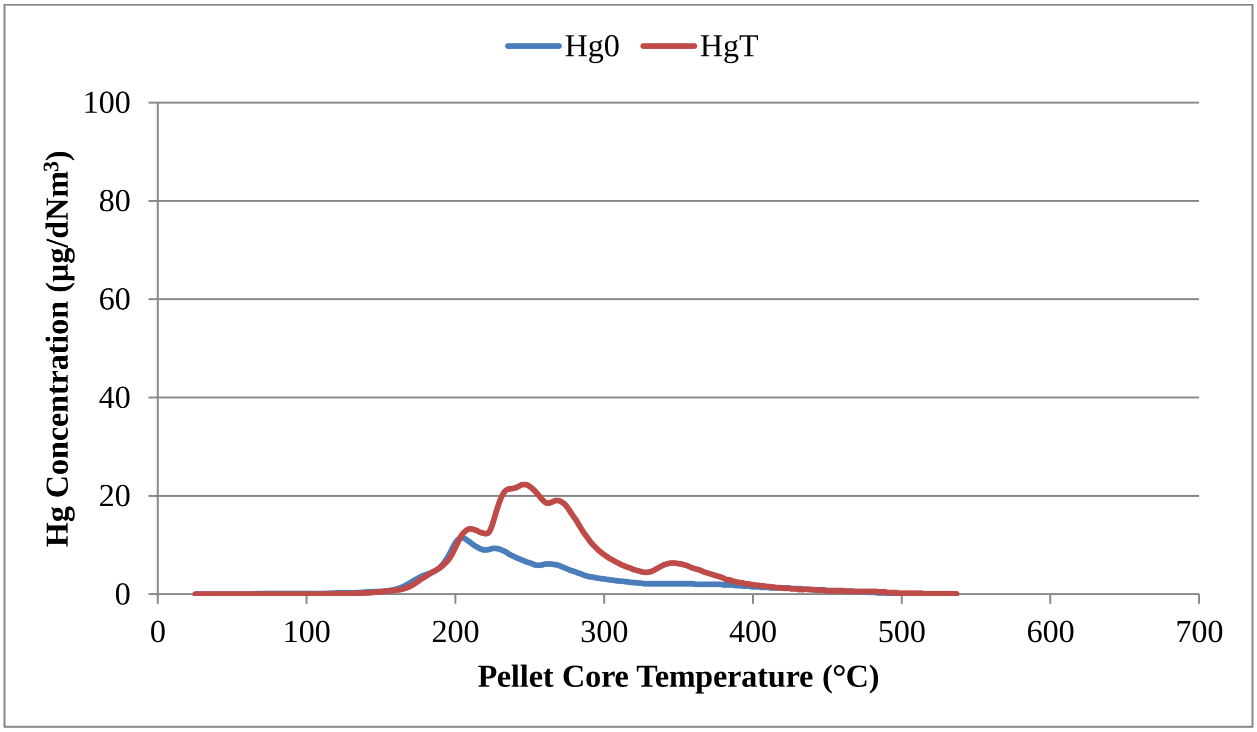

Figure 18. Mercury release profile for Keetac 0.5wt% run.

Hibtac Test Results

Results for Hibtac tests are found in Table 6 (standard green balls) and Table 7 (high compression green balls). For the standard green balls, results for different loadings showed slightly larger differences when compared to results of other plants, with differences also observed with the plots of individual runs for a particular loading as seen in Figures 19 to 21. Baseline runs averaged 17.1%, which is good agreement with the baselines of other plants. Runs for 0.1wt%, 0.5wt% and 0.5wt% replicate additive loadings averaged 54.6%, 60.9% and 56.7% respectively. The ESORB-HG-11 reduction potential estimated was 39.7% and 55.5% respectively.

The high compression green ball results showed good agreement with the standard green ball result (Table 7). The baseline runs averaged 16%, the 0.1wt% loading averaged 50% and the 0.5wt% loading averaged 63%. ESORB-HG-11 reduction potential was 39.7% and 55.5% for 0.1wt% and 0.5wt% respectively. The oxidation levels suggest no significant effect of the type of green ball (standard or high compression) on the oxidation capabilities of the added sorbent. Figures for the high compression green ball tests are presented in Appendix A.

The release profiles for the runs were also dissimilar, making a percentage mercury release plot not feasible as was the case with Utac and Keetac. The results however, show very good agreement with results for Minntac, Arcelor Mittal and Keetac.

Table 6. Results for Hibtac Standard Green Ball Testing.

Green Ball	Additive	Additive Loading	Observed Oxidation		Reduction Potential	
		(wt.%)	Test Runs (%)	Average	(%)	Average
Hibtac	ESORB-HG-11	Baseline	12.5 21.6 8.0	14.0	N/A	N/A
Hibtac	ESORB-HG-11	0.1	52.7 58.8 52.2	54.6	45.0 52.1 44.4	47.2
Hibtac	ESORB-HG-11	0.5	44.1 77.7	60.9	35.0 74.1	54.6
Hibtac	ESORB-HG-11	0.5	44.7 68.8	56.7	35.7 63.7	49.7

Table 7. Results for Hibtac High Compression Green Ball Testing.

Green Ball	Additive	Additive Loading (wt.%)	Observed Oxidation Test Runs (%)	Observed Oxidation Average	Reduction Potential (%)	Reduction Potential Average
Minntac	ESORB-HG-11	Baseline Replicate	15.1	10.1	N/A	N/A
			5.1			
Minntac	ESORB-HG-11	Baseline	22.0	22.6	N/A	N/A
			23.2			
Minntac	ESORB-HG-11	0.1	45.1	49.5	34.4	39.7
			47.6		37.4	
			55.9		47.3	
Minntac	ESORB-HG-11	0.5	46.8	62.8	36.4	55.5
			75.1		70.2	
			66.5		60.0	

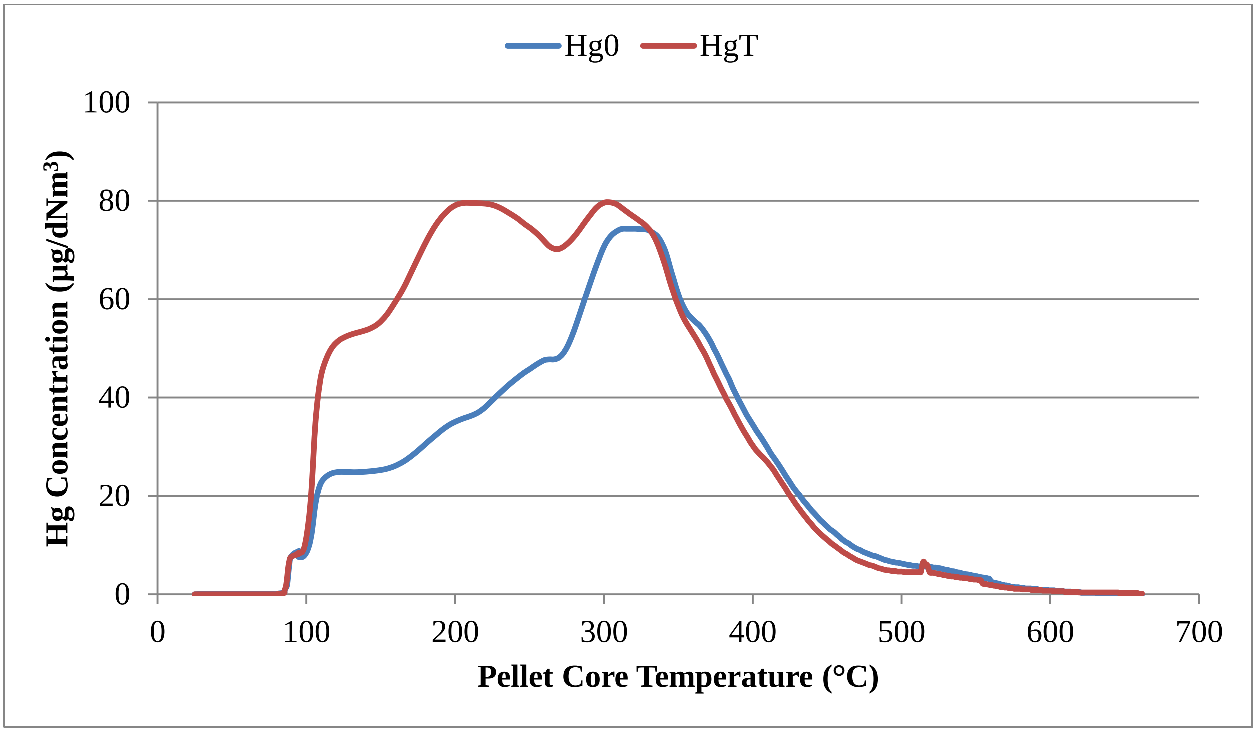

Figure 19. Mercury release profile for Hibtac standard green ball baseline run.

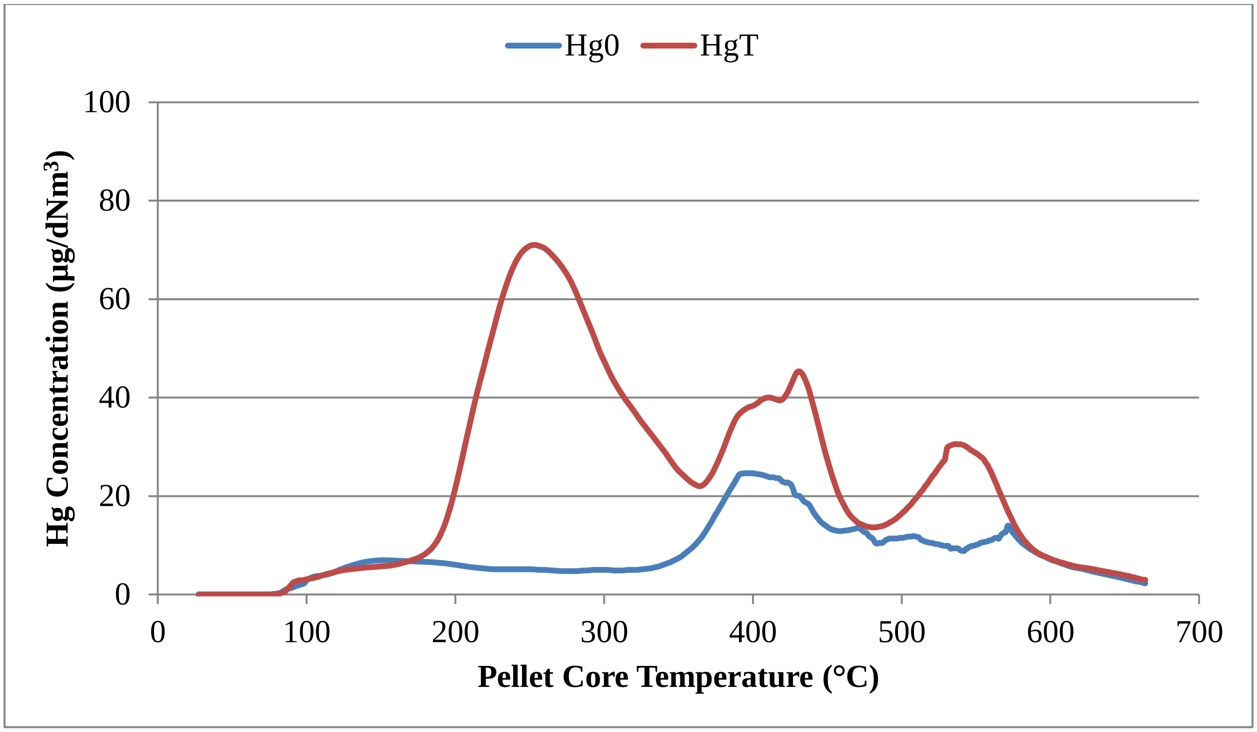

Figure 20. Mercury release profile for Hibtac standard green ball 0.1wt% run.

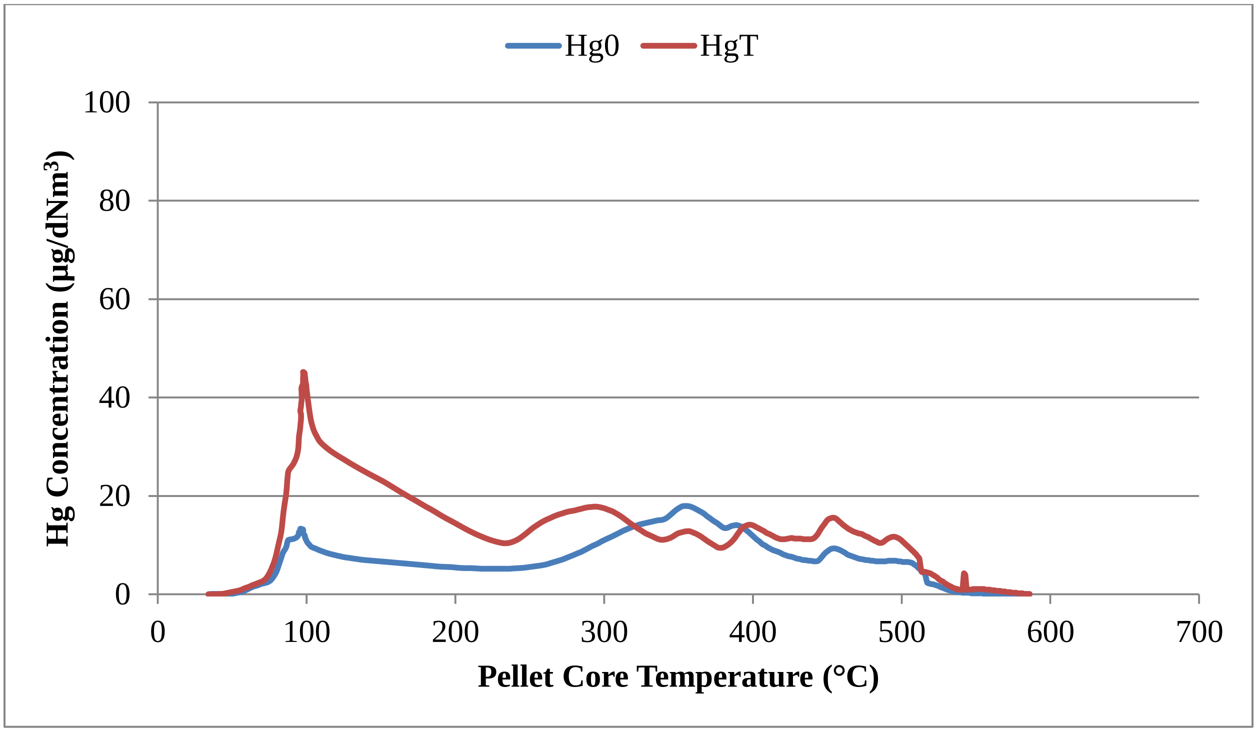

Figure 21. Mercury release profile for Hibtac standard green ball 0.5wt% run.

Additional Analyses

Additional analyses of green balls (unfired and fired) from Minntac (no carbon and 0.1wt%) and Utac were performed to possibly provide some insight into the mechanism involving mercury oxidation and/or release from the green balls as they were heated. Green ball samples at four different temperatures of 25°C (unheated), 400°C, 700°C and 1000°C were subjected to different analyses. Three of these analyses looked at the temperatures at which oxidation of magnetite occurs. Mössbauer spectroscopy provided qualitative and quantitative information on the type of iron oxide (hematite, magnetite or maghemite) present and their respective compositions. X-ray diffraction (XRD) is a qualitative analysis for identifying the compounds present in the different samples. Thermogravimetric analysis – Differential Scanning Calorimetry was used to determine mass change as a function of temperature, providing possible temperature at which oxidation starts. The samples were also analyzed to determine their mercury concentration.

Mercury concentration analysis of the samples was done using EPA method 7471 – Mercury in Solid or Semisolid Waste. The results are summarized in Table 8. The results obtained for the heated samples were either low or non-detect, and close to the method detection limit. This suggests that by 400°C most of the mercury associated with the initial green balls has been released, a trend that agrees with release data for almost all runs that show that 75% of the mercury is released by 400°C.

Table 8. Mercury Concentration in Green Balls Heated to Specific Temperatures.

	Additive Loading	Hg Concentration (ng/g) in GB at Temperature			
Green Ball	(wt.%)	25°C	400°C	700°C	1000°C
Minntac	0	6.6	ND	ND	ND
Minntac	0.1	25	5.2	5.0	ND
Utac	0.1	26	5.9	ND	ND

ND = Non detect; NA = Not analyzed.

Mössbauer results, Table 9 to 11, identified Hematite in small concentrations present in the 400°C sample (largest concentration identified was 22%) and increasing. For the 1000°C sample only hematite (not shown in tables) was identified. The 400°C temperature is the temperature of the pellet core, meaning the surface of the pellet is at an even higher temperature. This suggests that magnetite oxidation by hematite starts at around 400°C, an observation also seen in the TGA-DSC and XRD results. Mössbauer results did not conclusively identify the maghemite to be present in the any of the samples; however, the data seemed to suggest the possible presence of maghemite in the 400°C and 700°C sample. Maghemite has been identified in partially fired green ball samples collected under the induration grate of some of the taconite facilities. It is also believed to play a role in the oxidation of mercury in taconite processes [Berndt et al, 2005].

TGA analysis, Figures 22 and 23, consisted of heating the samples to 1100°C in air at a ramp rate of 20°C/min and held at 1100°C for 10 min. Two significant drops in weight were observed at the start of the heating and also at 700°C. The first drop was attributed to moisture loss. The second drop was considered to be due to calcination of carbonate species (limestone or dolomite) present in the sample. A significant drop was not observed in the Utac sample, most likely due to the low level of limestone used in Utac green ball formulations. Heating the samples in nitrogen to 800°C followed by heating in air showed only a mass increase which started between 350°C and 400°C. This same increase can also be seen in the samples heated in air. This confirms the observation made in the Mössbauer analysis that oxidation to hematite starts around 400°C.

Finally, XRD analysis showed an increase in hematite concentration from 400°C to 1000°C agreeing with the Mössbauer results. The XRD results (not shown) also confirmed that the disappearance of carbonate species for the 1000°C sample, confirming the observation that the weight loss seen in the TGA-DSC analysis is due to calcination of carbonate species.

The most important observation from these additional analyses is the fact that the oxidation of magnetite to hematite seems to begin at around 400°C with less than 25% mercury observed in the 400°C samples. Meanwhile, by 400°C, 75% of the mercury has been released for more than 80% of the runs performed. This agrees with work done by Benner [2003] who also observed that most of the mercury associated with green balls is out by 400°C. This would suggest that the mercury release from the green balls during the bench tests is not a function of the magnetite oxidation to hematite. Previous work performed by Berndt [2005] suggested that the oxidation of the magnetite in green balls to a maghemite/magnetite solution followed by hematite plays a role in the capture/release/oxidation of mercury in taconite facilities. Air flow patterns in taconite facilities are a lot more complex than those involved in the bench tests. Air from a hotter section of the processes is usually used to heat up colder sections, meaning mercury released in the system re-contacts the green balls and might explain the different conclusions observed between these bench tests and previous field work.

Table 9. Mössbauer Results for Utac Samples Containing 0.1wt% ESORB-HG-11.

Sample	I.D.	Magnetite A/B Ratio	Percent Total
Baseline	Magnetite A	0.62	36.89
	Magnetite B		46.60
	Magnetite B		12.62
	Unknown		3.88
Total			100.00
400°C	Magnetite A	0.60	28.00
	Magnetite B		41.00
	Magnetite B		6.00
	Hematite		21.00
	Unknown		4.00
Total			100.00
700°C	Magnetite A	0.95	18.81
	Magnetite B		13.86
	Magnetite B		5.94
	Hematite		58.42
	Unknown		2.97
Total			100.00

Table 10: Mössbauer Results for Heated Minntac Samples not Containing ESORB-HG-11

Sample	I.D.	Magnetite A/B Ratio	Percent Total
Baseline	Magnetite A	0.73	40.57
	Magnetite B		50.71
	Magnetite B		5.07
	Unknown		3.65
Total			100.00
400°C	Magnetite A	0.65	32.97
	Magnetite B		44.82
	Magnetite B		5.98
	Hematite		12.95
	Unknown		3.39
Total			100.00
700°C	Magnetite A	1.0	27.72
	Magnetite B		21.78
	Magnetite B		5.94
	Hematite		44.55
Total			100.00

Table 11. Mössbauer Results for Heated Minntac Samples Containing 0.1wt% ESORB-HG-11.

Sample	I.D.	Magnetite A/B Ratio	Percent Total
Baseline	Magnetite A	0.4	40.82
	Magnetite B	0.48	48.98
	Magnetite B	0.07	7.14
	Unknown	0.03	3.06
Total		0.98	100.00
400°C	Magnetite A	0.31	30.88
	Magnetite B	0.4	39.84
	Magnetite B	0.09	8.96
	Hematite	0.17	16.93
	Unknown	0.034	3.39
Total		1.004	100.00
700°C	Magnetite A	0.28	28.28
	Magnetite B	0.21	21.21
	Magnetite B	0.06	6.06
	Hematite	0.44	44.44
Total		0.99	100.00

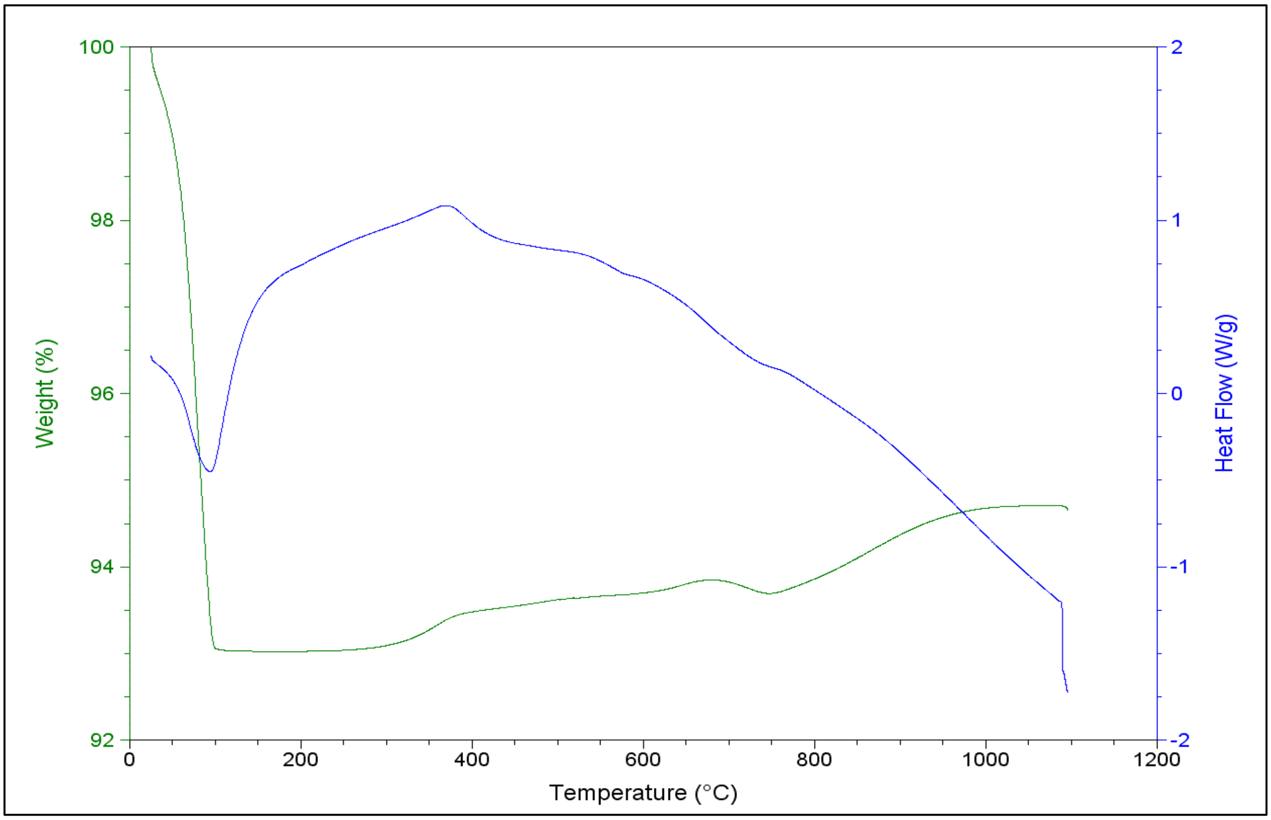

Figure 22. TGA-DSC curve for carbon-containing Utac green ball.

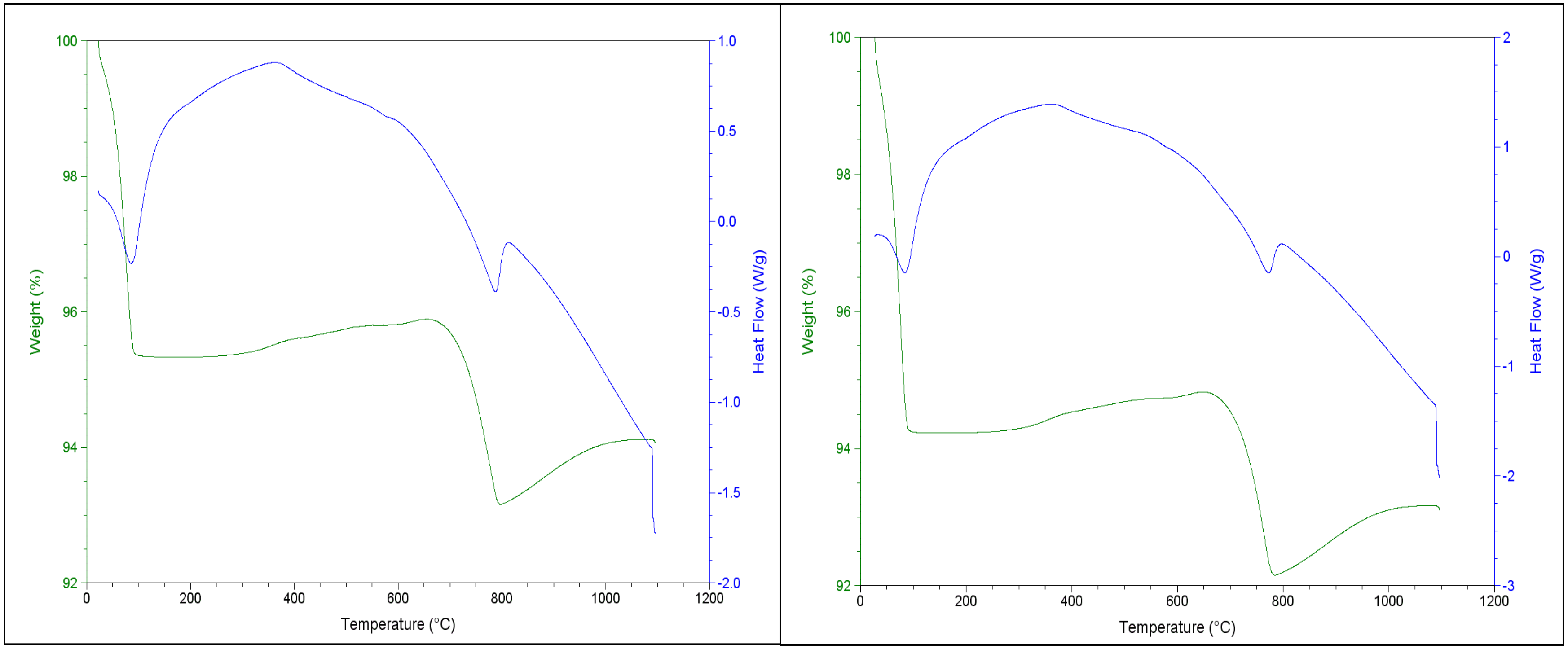

Figure 23. a) TGA-DSC curve for carbon-free Minntac green balls. b) TGA-DSC curve for carbon-containing Minntac green balls.

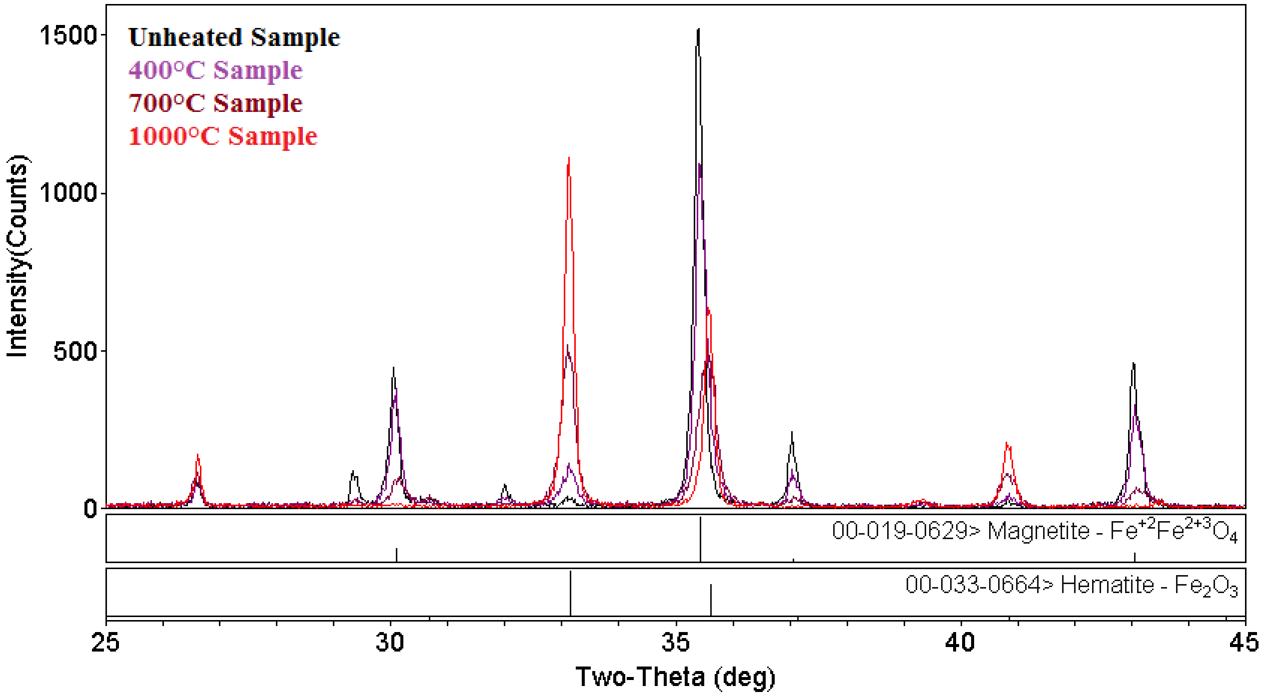

Figure 24. XRD results for Utac green ball sample at a) baseline b) 400°C c) 700°C, and d) 1000°C.

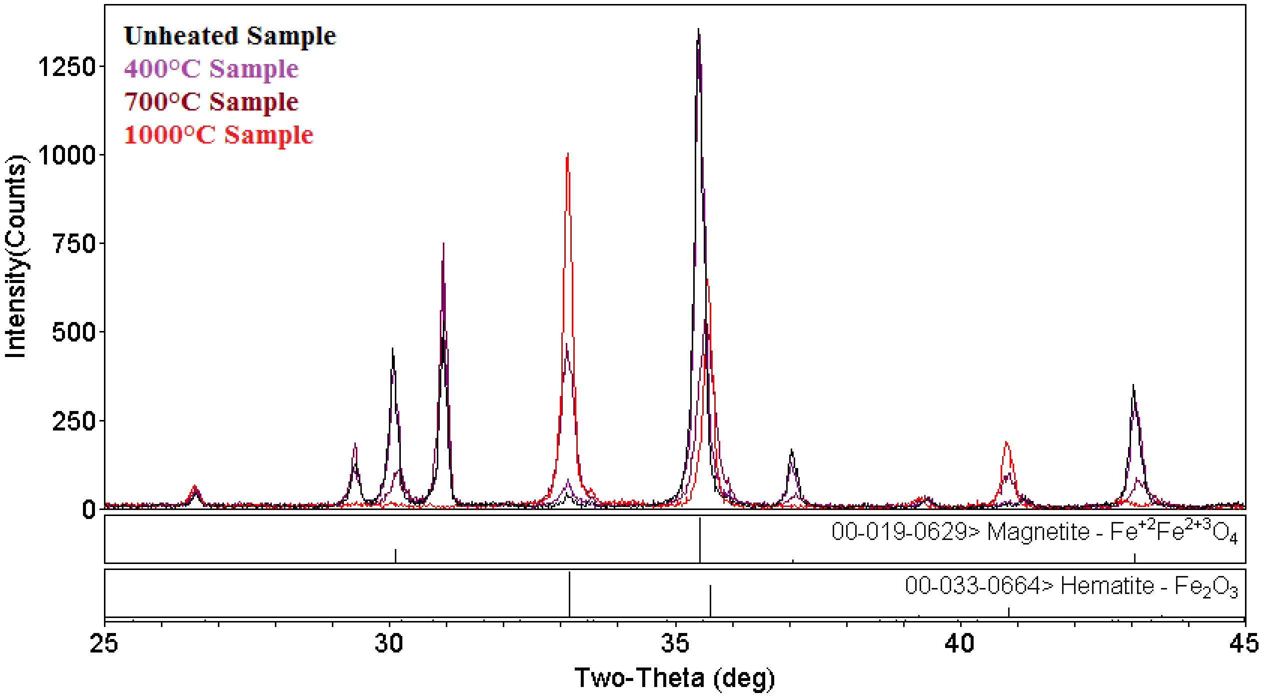

Figure 25. XRD results for Minntac green ball with no carbon at a) baseline b) 400°C c) 700°C, and d) 1000°C.

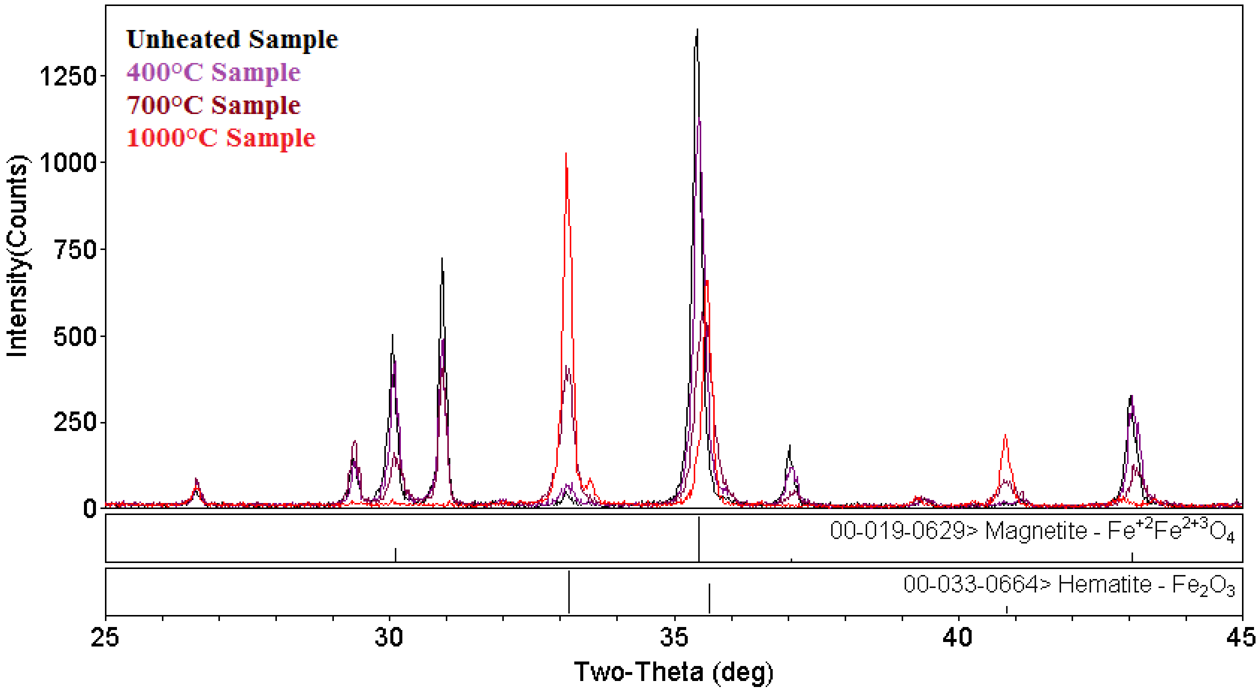

Figure 26. XRD results for Minntac green ball with 0.1wt% carbon at a) baseline b) 400°C c) 700°C, and d) 1000°C.

SEM analysis was aimed at observing how oxidation of magnetite to hematite was propagated as the green ball was heated. Samples analyzed using SEM were ground down to a 200 mesh size and suspended in an epoxy resin to enable polishing of the sample using a diamond polishing wheel. The images obtained, Figure 24, didn't show any observable difference on the surface of the iron particles. Forsmo suggested that oxidation of magnetite to hematite occurs from the surface of the particle first with oxidation of magnetite in the core controlled by the diffusion of oxygen into the particle lattice. This could explain why the SEM images obtained do not show any discernible magnetite or hematite.

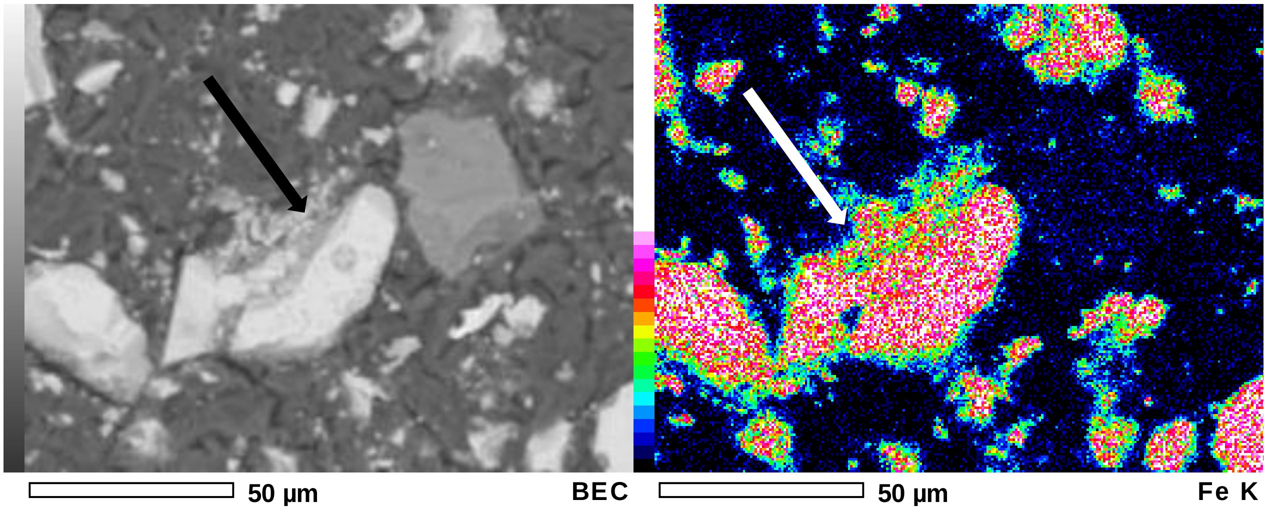

Figure 27. Carbon-containing Minntac 400°C sample showing a) SEM image magnified at 700x. b) Back scattered analysis of SEM image showing presence of iron. No discernible difference on iron surface.

Conclusions

Testing of green balls for all five Taconite facilities operating on the Mesabi Iron Range demonstrated that the additive – ESORB-HG-11 (a brominated activated carbon) has the ability to improve mercury oxidation as the mercury thermally desorbs. Green balls containing ESORB-HG-11 showed oxidation due to the additive alone (or, mercury reduction potential – using a scrubber to capture oxidized mercury) ranging from 29% to 74%, except for green balls obtained from United Taconite. Average oxidation values obtained for all plants are presented in Figure 28.

Baseline oxidations gave an average of 18% for all the runs, with a standard deviation of 6%. Additive loadings of 0.1wt% gave a reduction potential of 42% with a standard deviation of 9%, and, additive loading of 0.5wt% gave a reduction potential of 48% with a standard deviation of 13%. United Taconite data were not included in determining averages. The close agreement between results of different plants confirms that ESORB-HG-11 is effective in promoting mercury oxidation. The mercury oxidation observed for ESORB-HG-11 – containing green balls is considered to occur as a solid phase reaction on the surface of the green ball pellets. Gas phase oxidation reactions are not considered significant during the bench testing. This implies that there is a potential for higher oxidation levels to be observed for full-scale testing of the technology, as previous testing at taconite facilities [Berndt, Engesser 2005] suggest that gas phase mercury oxidation contributes to the final oxidation observed. Moreover, ESORB-HG-11 has proven to show good gas phase oxidation capabilities when tested at Minntac line 3 [Taconite Mercury Emission Control Studies - Project 1].

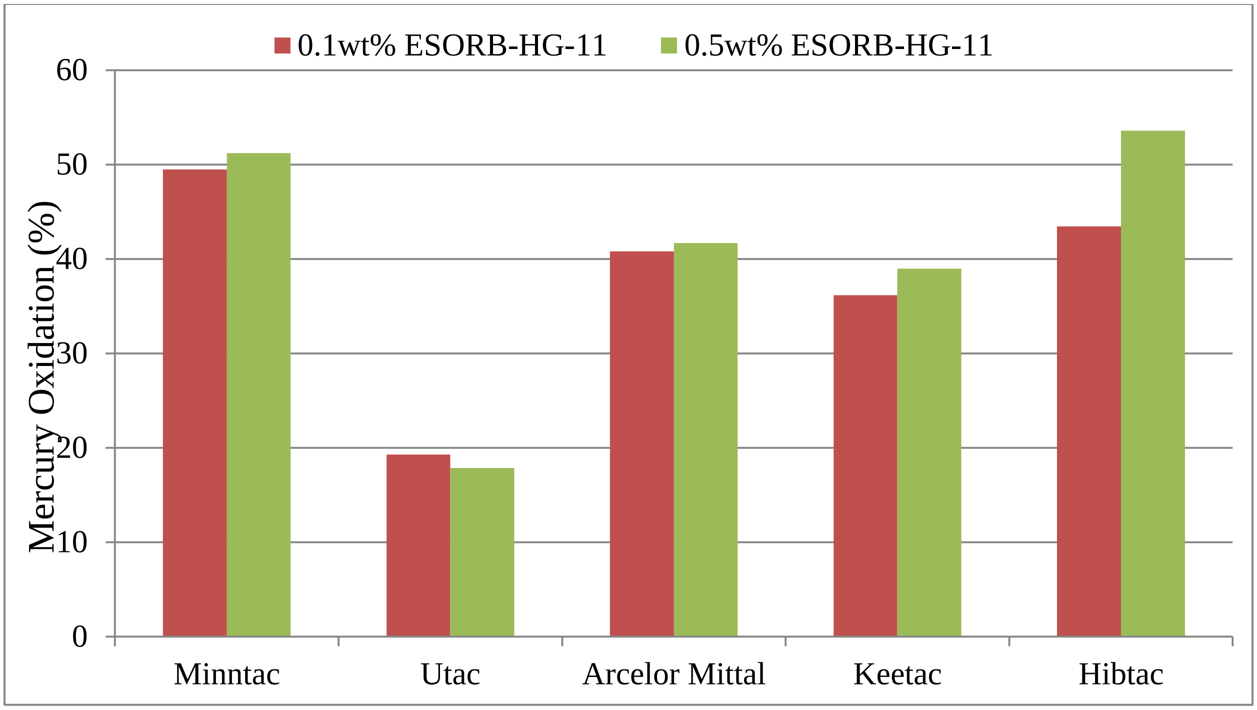

Figure 28. Reduction potential observed for 0.1wt% and 0.5wt% loading of ESORB-HG-11.

The green balls tested were produced by the Coleraine Minerals Research Laboratory (CMRL) of the Natural Resources Research Institute (NRRI) and were subjected to industry-standard, Batch Balling tests to evaluate the effect the additive had on the moisture content, wet drop number, and dry compressive strength. For the samples with 0.1weight% additive, no significant difference due to addition of ESORB-HG-11 was observed with respect to the baseline standard during the batch balling tests. Slight differences from the baseline standard were observed with the 0.5weight% additive loading. The 0.1weight% loading was determined to be the optimum loading for potential full-scale testing of the technology.

Future Work

Suggested future work for this project primarily consists of conducting Fired Pellet Quality Tests on carbon-containing green balls to ensure that addition of ESORB-HG-11 to the green ball does not affect the physical properties of the taconite pellets.

If the tests confirm that addition of ESORB-HG-11 to green balls has no significant negative effect on the physical properties of the taconite pellets, then full-scale testing of the technology is recommended to determine actual reduction potential.

References

Benner, B. (2005) *Mercury release from taconite during heating*. CMRL report TR-05-06/NRRI/TR-2005-17, 3 pages.

Berndt, M. E. *Mercury and Mining in Minnesota*, Report, MN Dept. of Natural Resources, 2003.

Berndt, M.E.; Engesser, J. E. *Mercury Transport in Taconite Processing Facilities: (II) Release and Capture during Induration*, Report, MN Dept. of Natural Resources, 2005.

Berndt, M. E.; Engesser, J. E. *Mercury Transport in Taconite Processing Facilities: (III) Control Method Test Results*, Report, MN Dept. of Natural Resources, 2007.

Berndt, M. E.; Engesser, J. E.; Berquó, T. S. *Mercury Chemistry and Mössbauer Spectroscopy of Iron Oxides During Taconite Processing on Minnesota's Iron Range*, Report, MN Dept. of Natural Resources, 2005b.

Environmental Protection Agency, *AP 42: Compilation of Air Pollutant Emission Factors*, CH. 11, Volume 1, Fifth Edition; http://www.epa.gov/ttnchie1/ap42/ch11/final/c11s23.pdf (Accessed June 10, 2012).

Forsmo, S. *Influence of Green Pellet Properties on Pelletizing of Magnetite Iron Ore*, Doctoral Thesis, Luleå University of Technology, Luleå, Sweden, 2007.

Galbreath, K. C. *Mercury Vaporization Characteristics of Taconite Pellets*, Final Report, MN Dept. of Natural Resources, 2005.

QAPP for Taconite Mercury Control Studies: Phase 1, Minnesota Department of Natural Resources, 2010.

Appendix A – Results

Minntac Baseline Results:

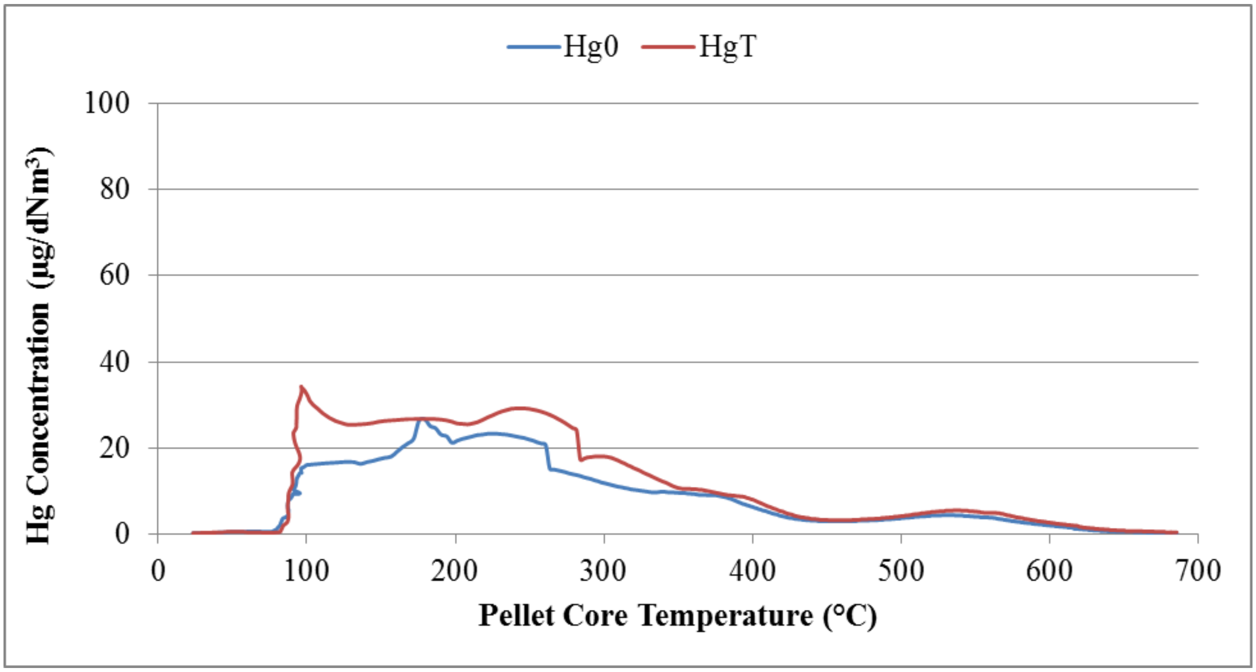

Figure 29. Mercury release profile for Minntac second baseline run.

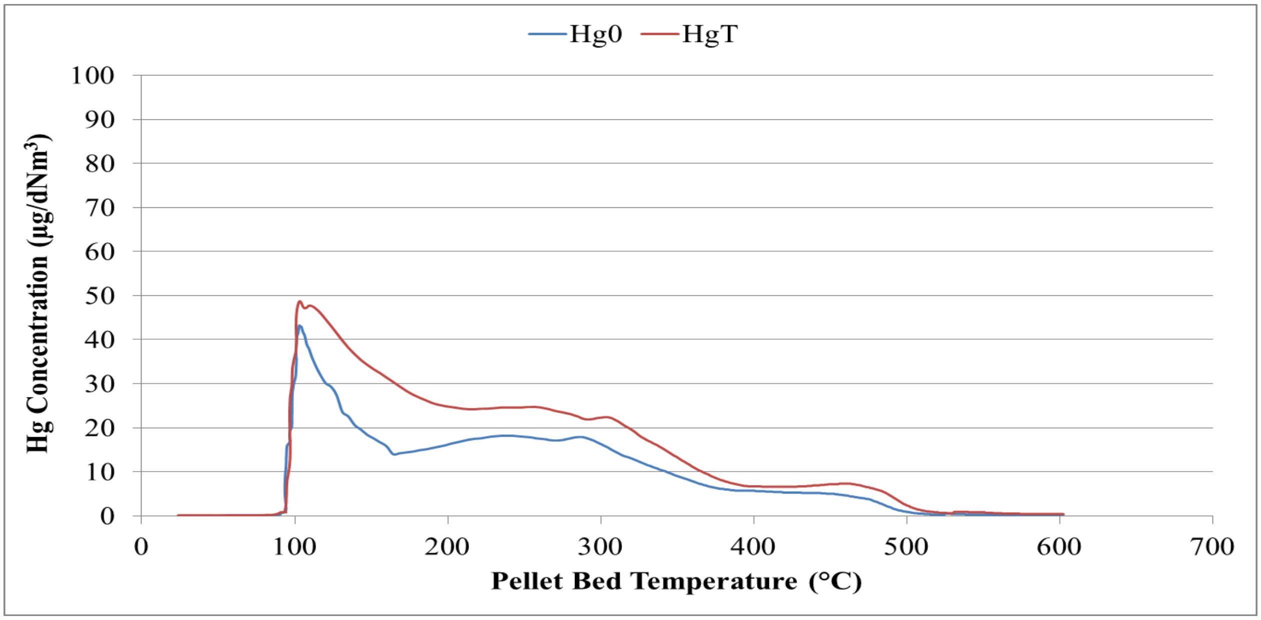

Figure 30. Mercury release profile for Minntac replicate batch first baseline run.

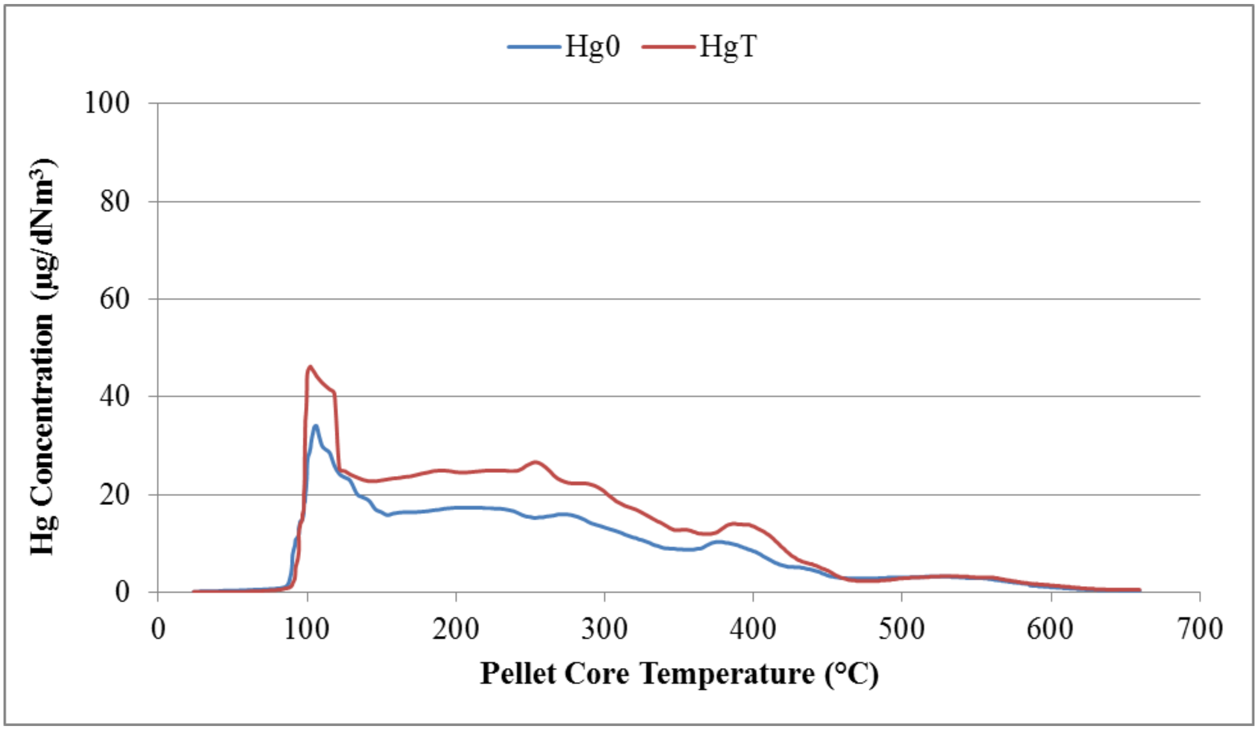

Figure 31. Mercury release profile for Minntac replicate batch second baseline run.

Minntac 0.1wt% Loading Runs:

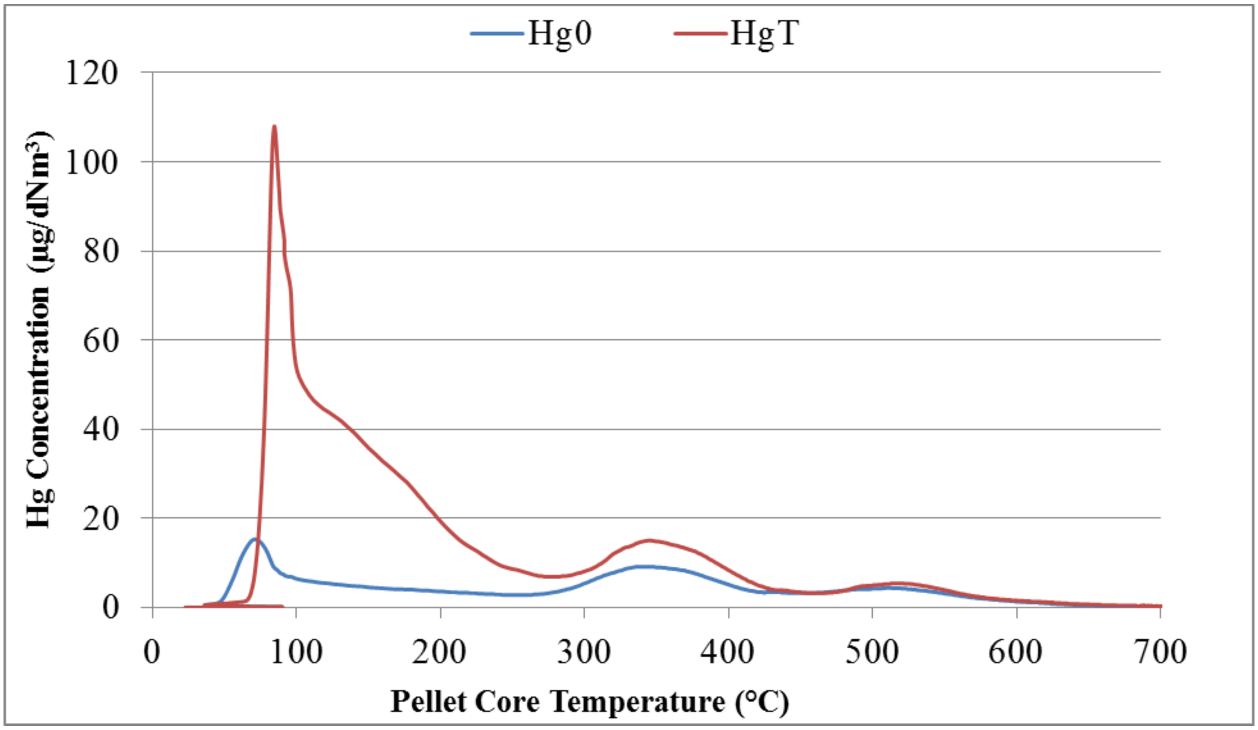

Figure 32. Mercury release profile for Minntac second 0.1wt% run.

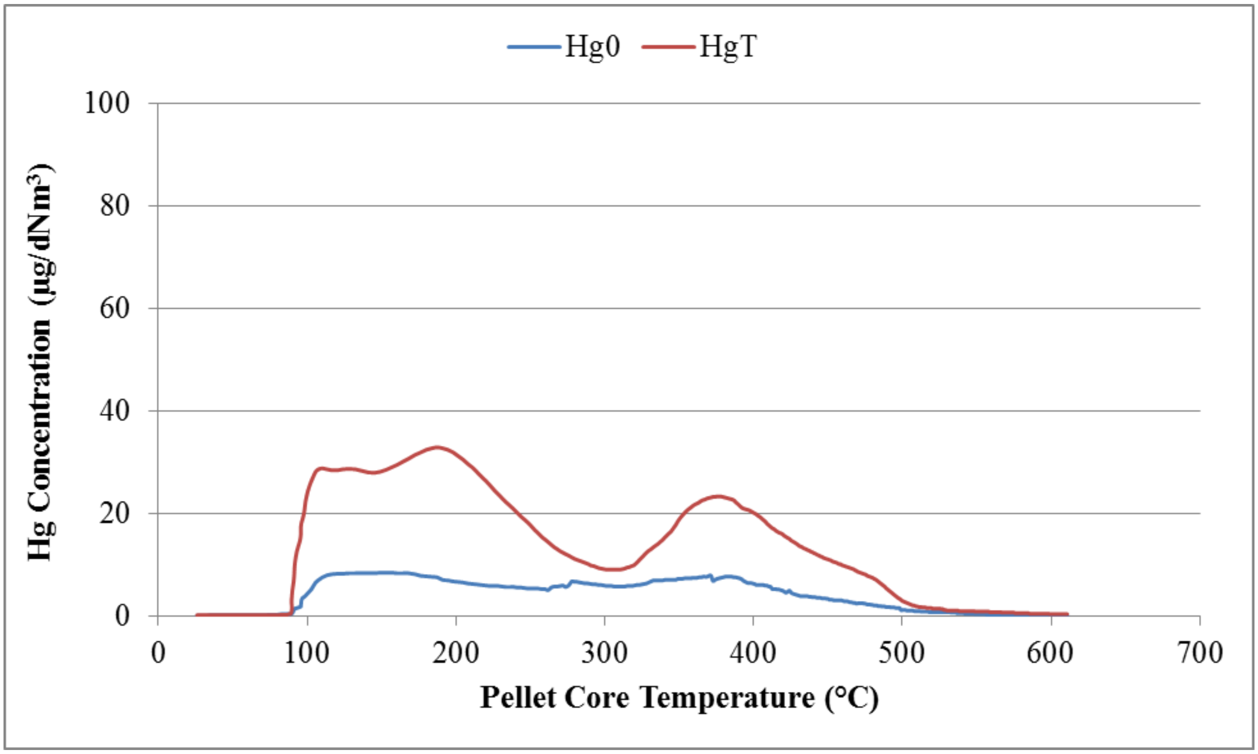

Figure 33. Mercury release profile for Minntac third 0.1wt% run.

Minntac 0.5wt% Loading Results:

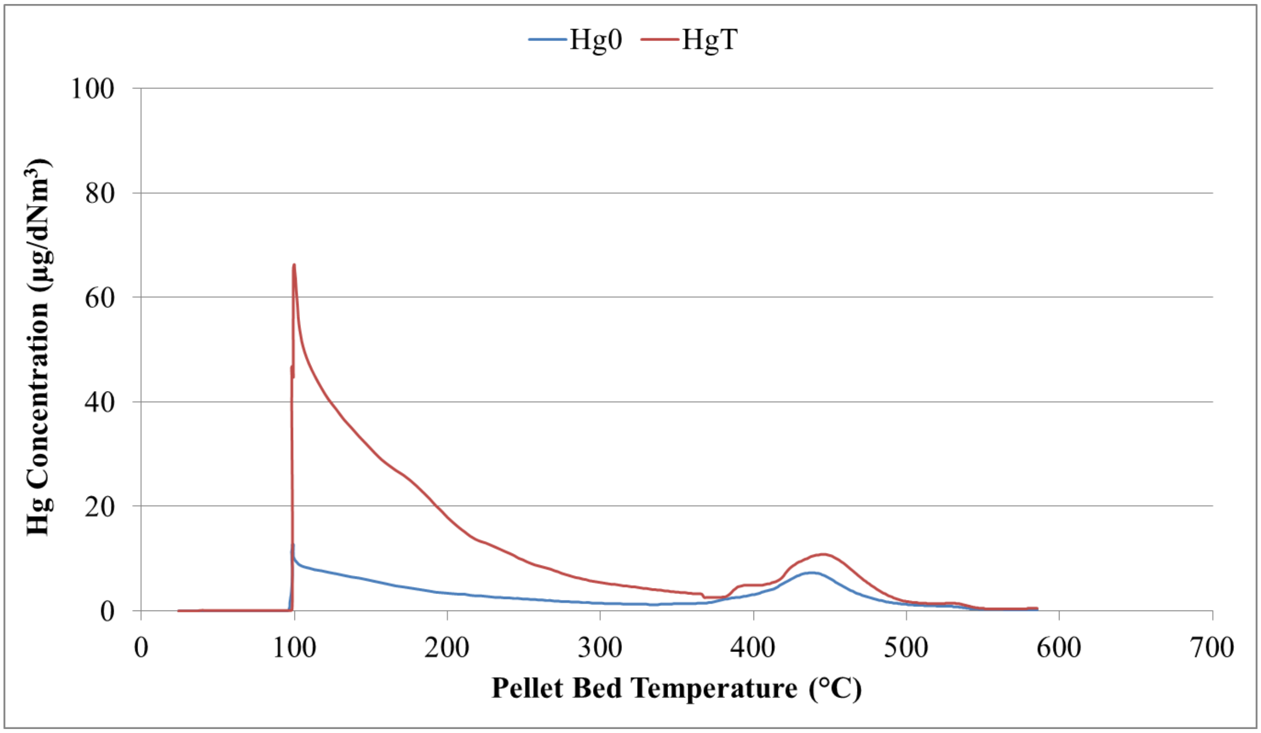

Figure 34. Mercury release profile for Minntac first 0.5wt% run.

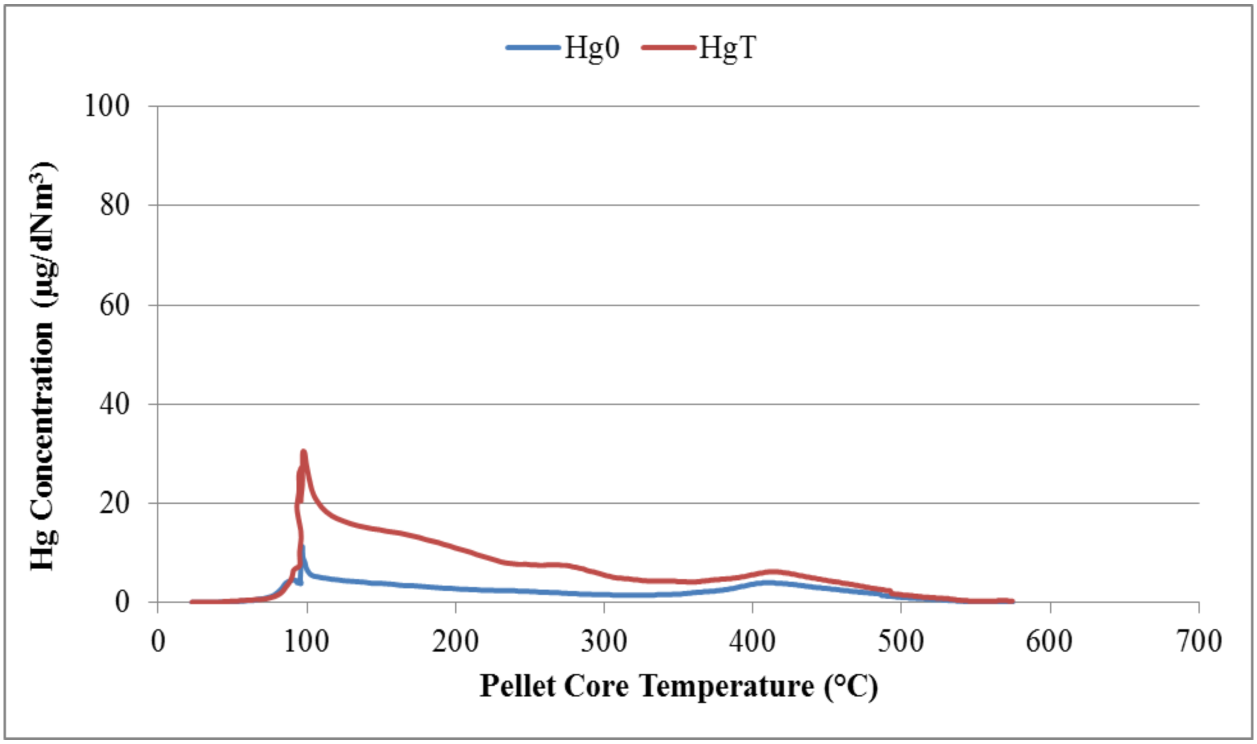

Figure 35. Mercury release profile for Minntac second 0.5wt% run.

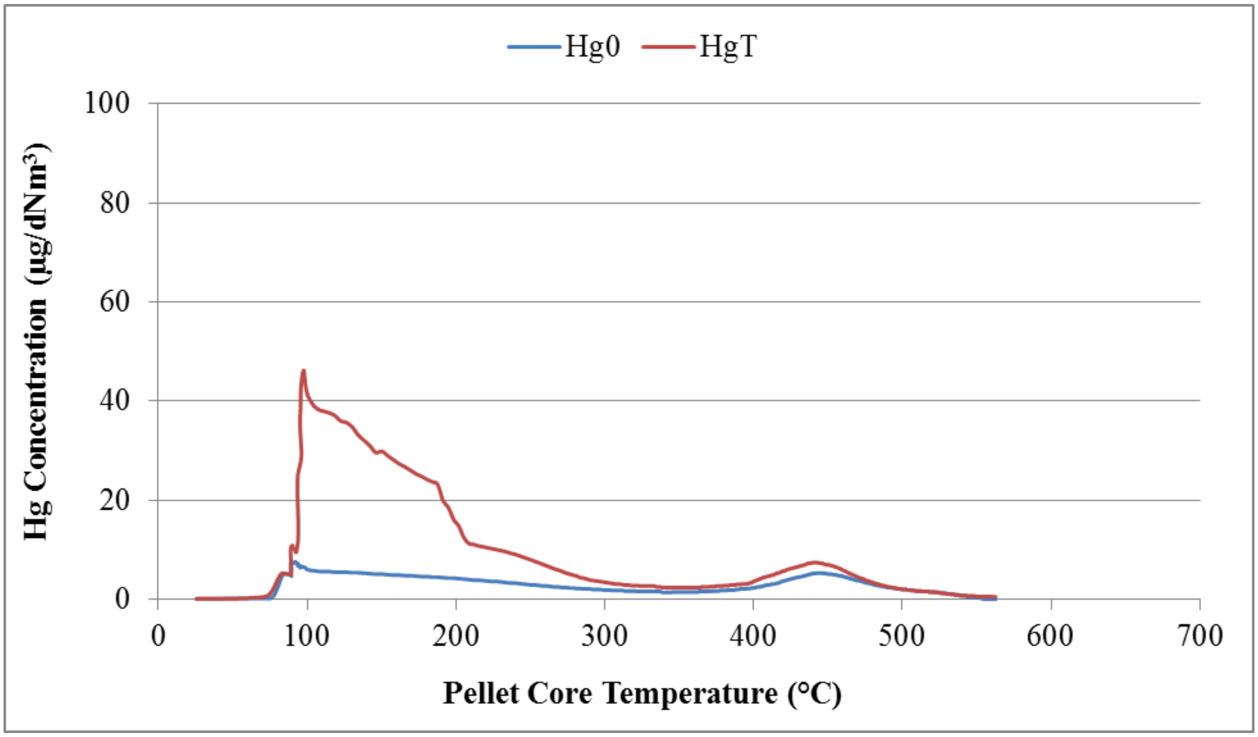

Figure 36. Mercury release profile for Minntac third 0.5wt% run.

Utac Baseline Results:

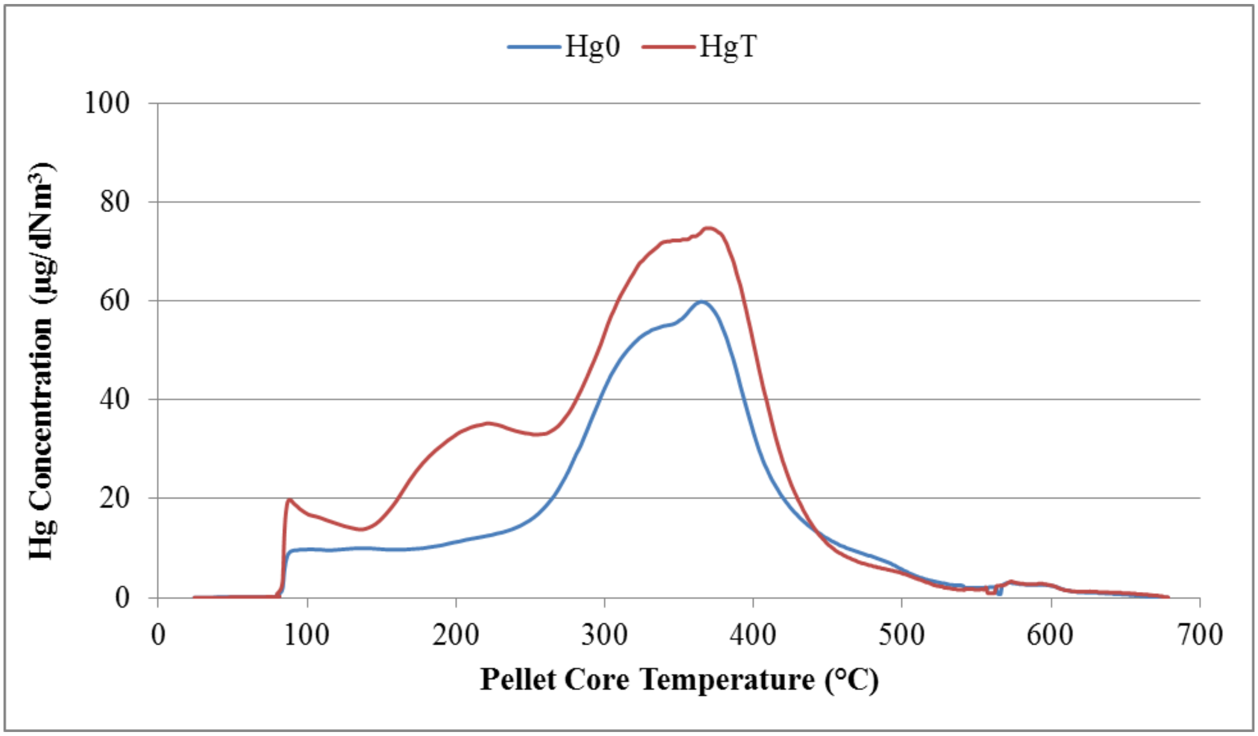

Figure 37. Mercury release profile for Utac first baseline run.

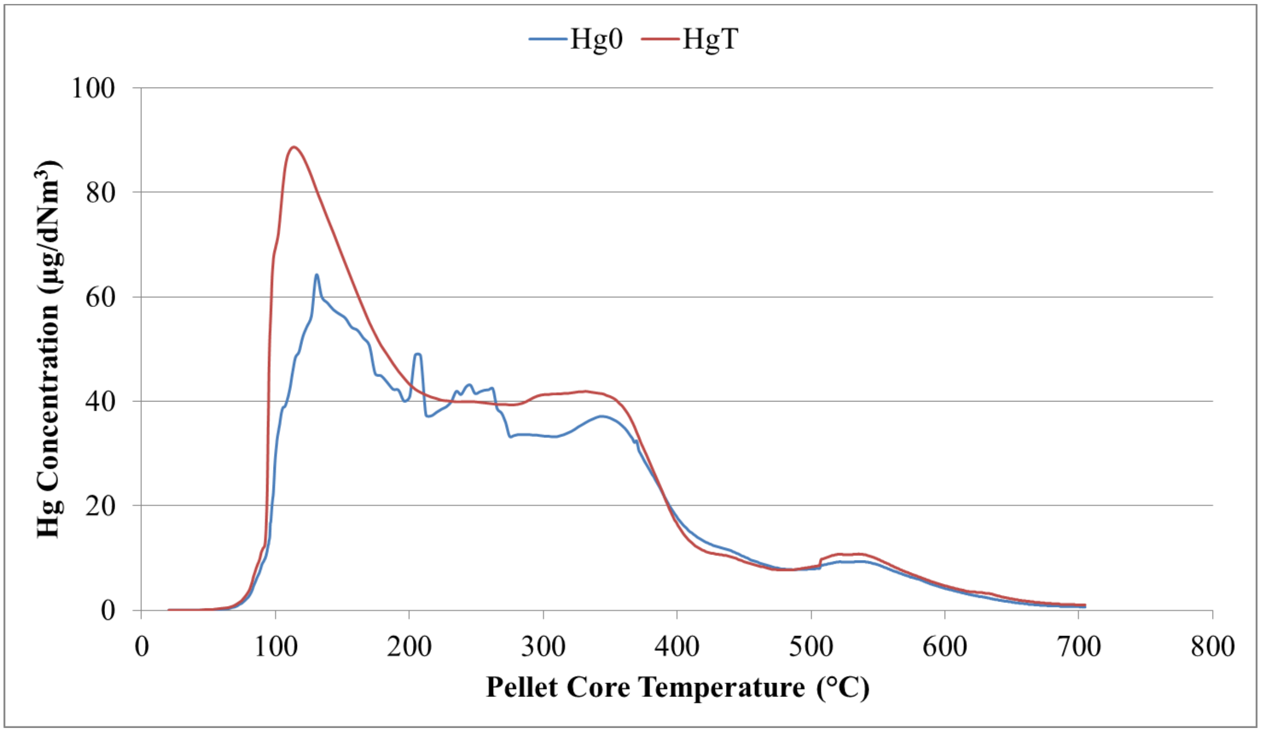

Figure 38. Mercury release profile for Utac third baseline run.

Utac 0.1wt% Loading Results:

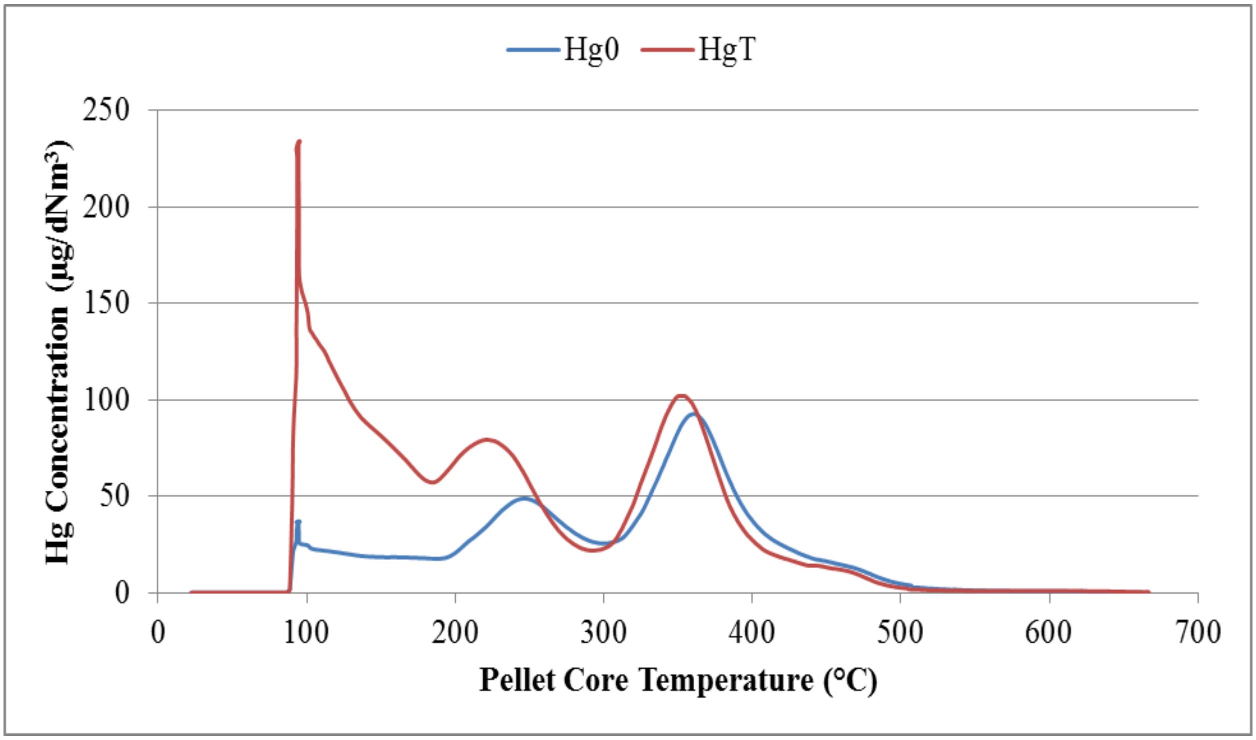

Figure 39. Mercury release profile for Utac third 0.1wt% run.

Utac 0.5wt% Loading Results:

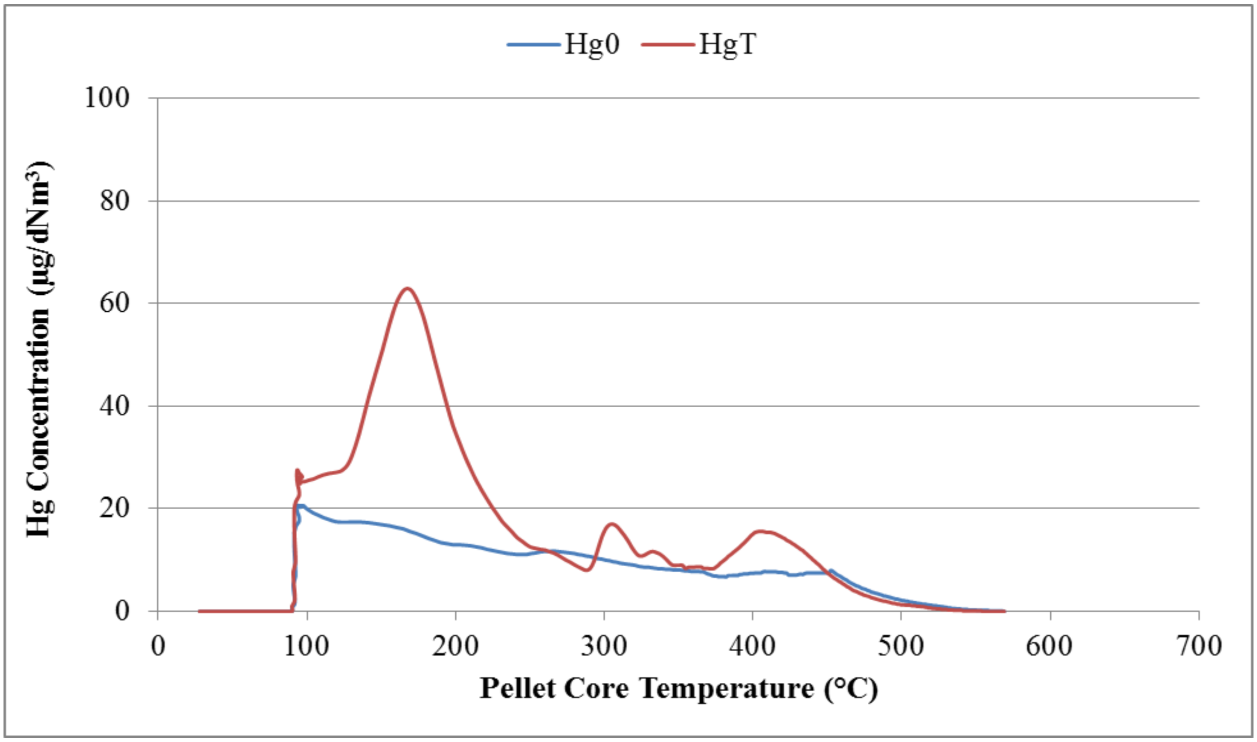

Figure 40. Mercury release profile for Utac first 0.5wt% run.

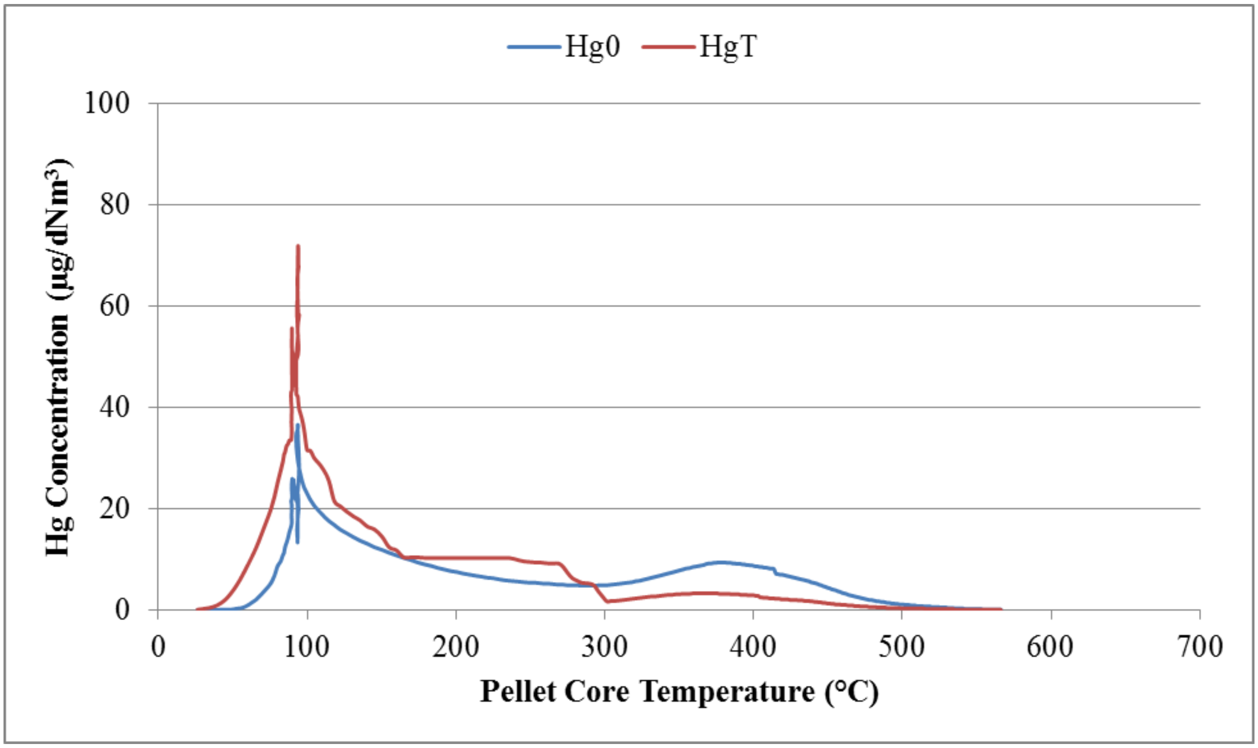

Figure 41. Mercury release profile for Utac second 0.5wt% run.

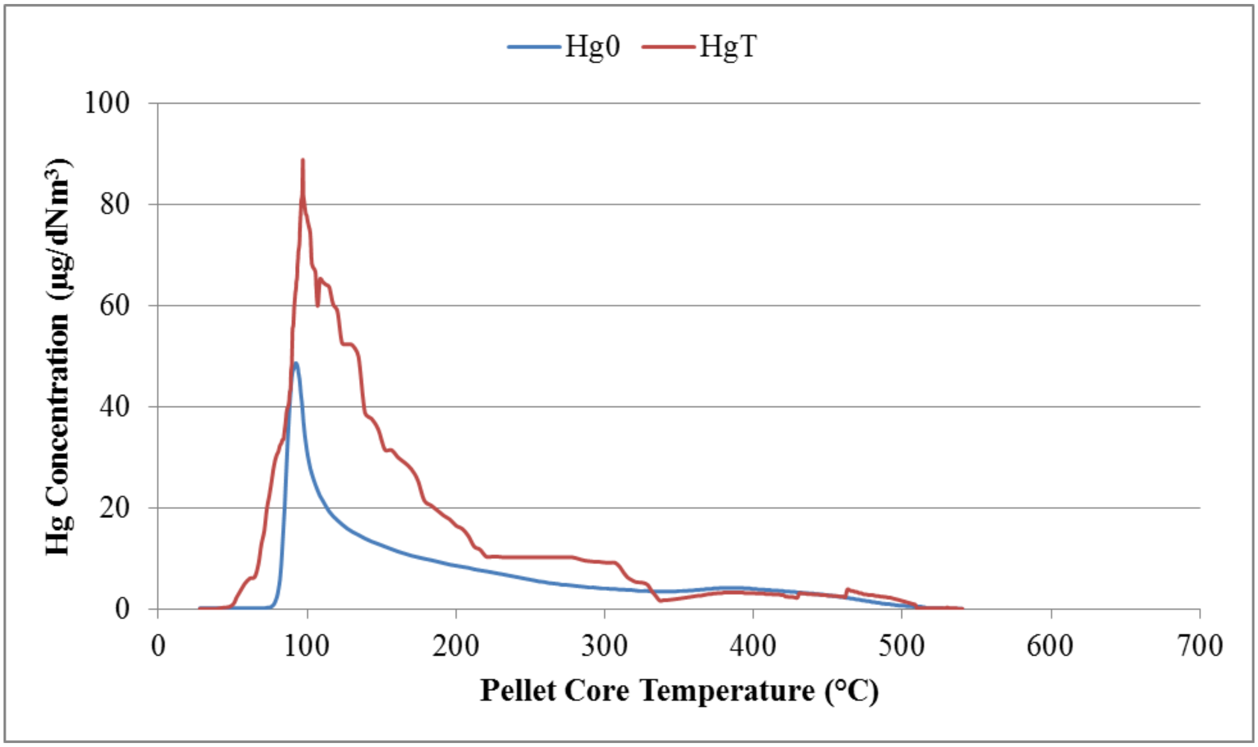

Figure 42. Mercury release profile for Utac replicate second 0.5wt% run.

Arcelor Mittal Baseline Results:

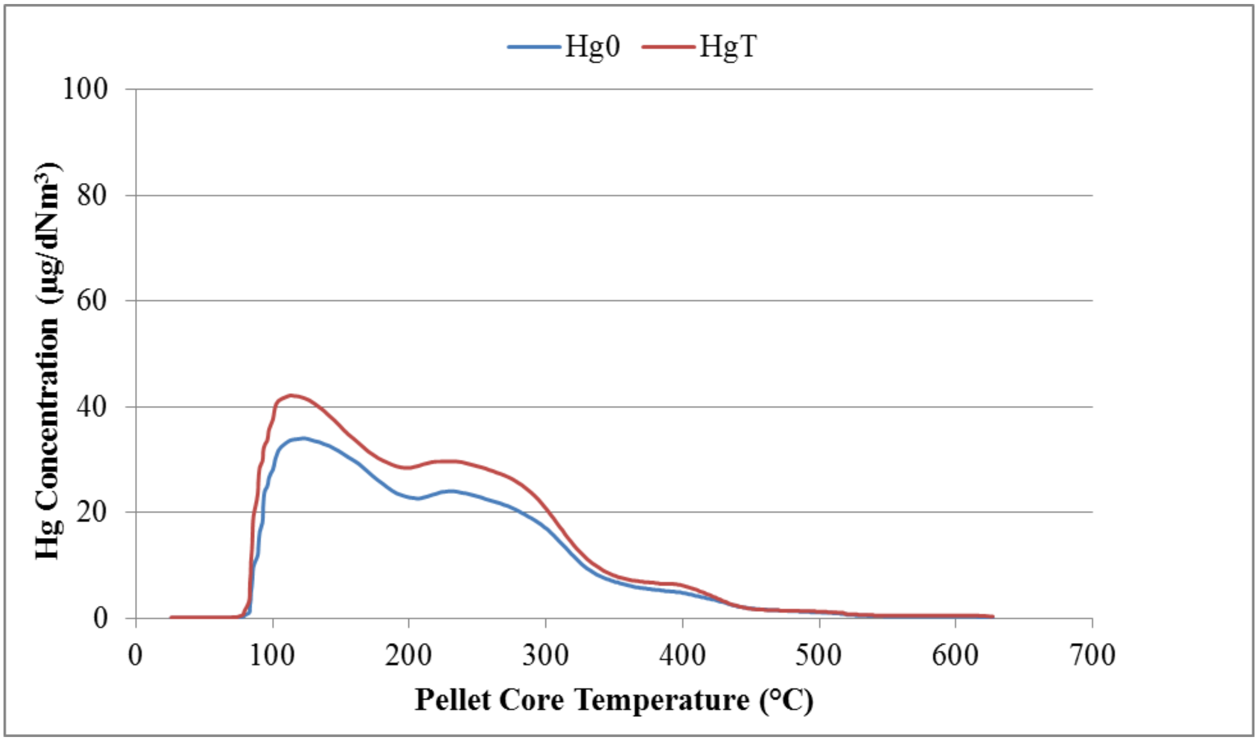

Figure 43. Mercury release profile for Arcelor Mittal baseline run.

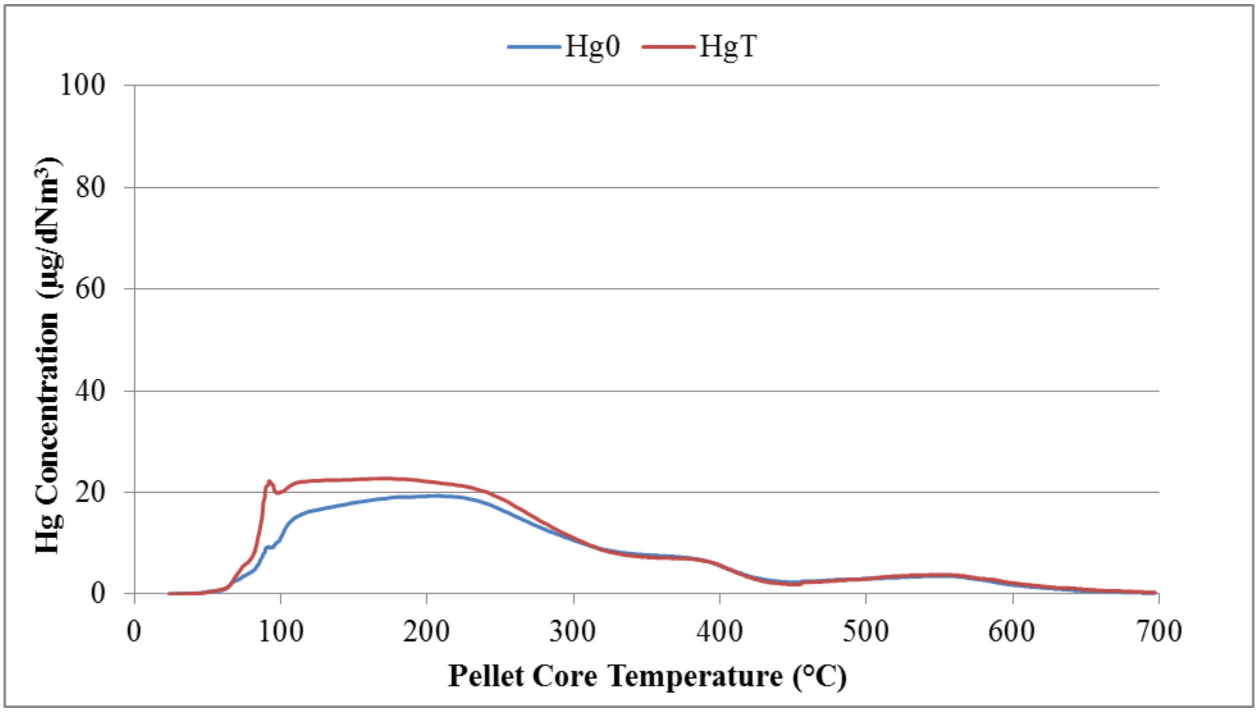

Figure 44. Mercury release profile for Arcelor Mittal third baseline run.

Arcelor Mittal 0.1wt% Loading Results:

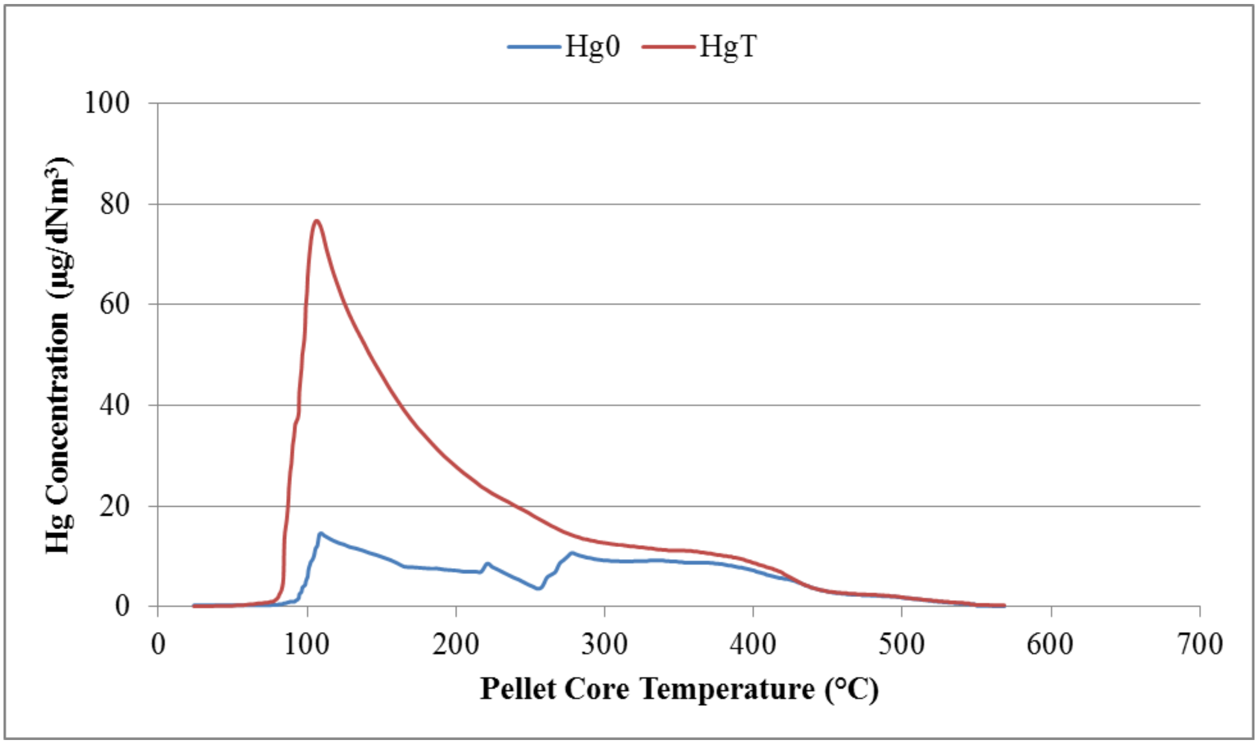

Figure 45. Mercury release profile for Arcelor Mittal first 0.1wt% loading run.

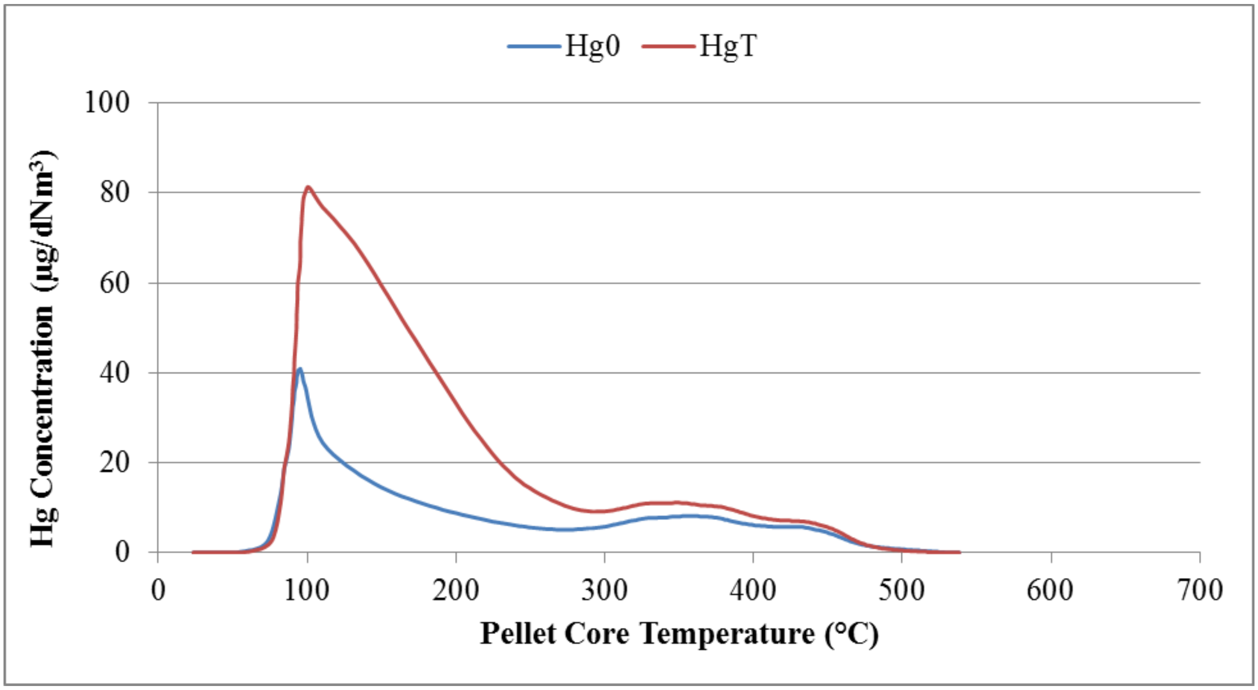

Figure 46. Mercury release profile for Arcelor Mittal second 0.1wt% loading run.

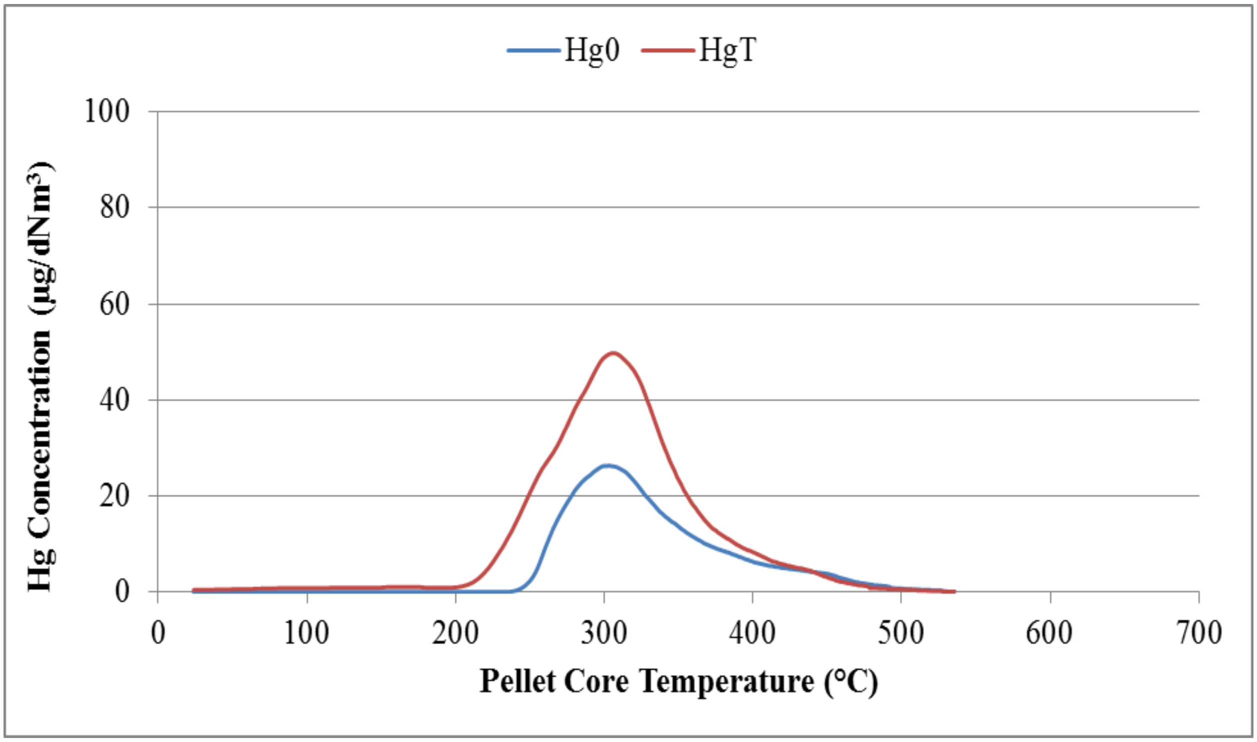

Figure 47. Mercury release profile for Arcelor Mittal second 0.1wt% replicate loading run.

Arcelor Mittal 0.5wt% Loading Results:

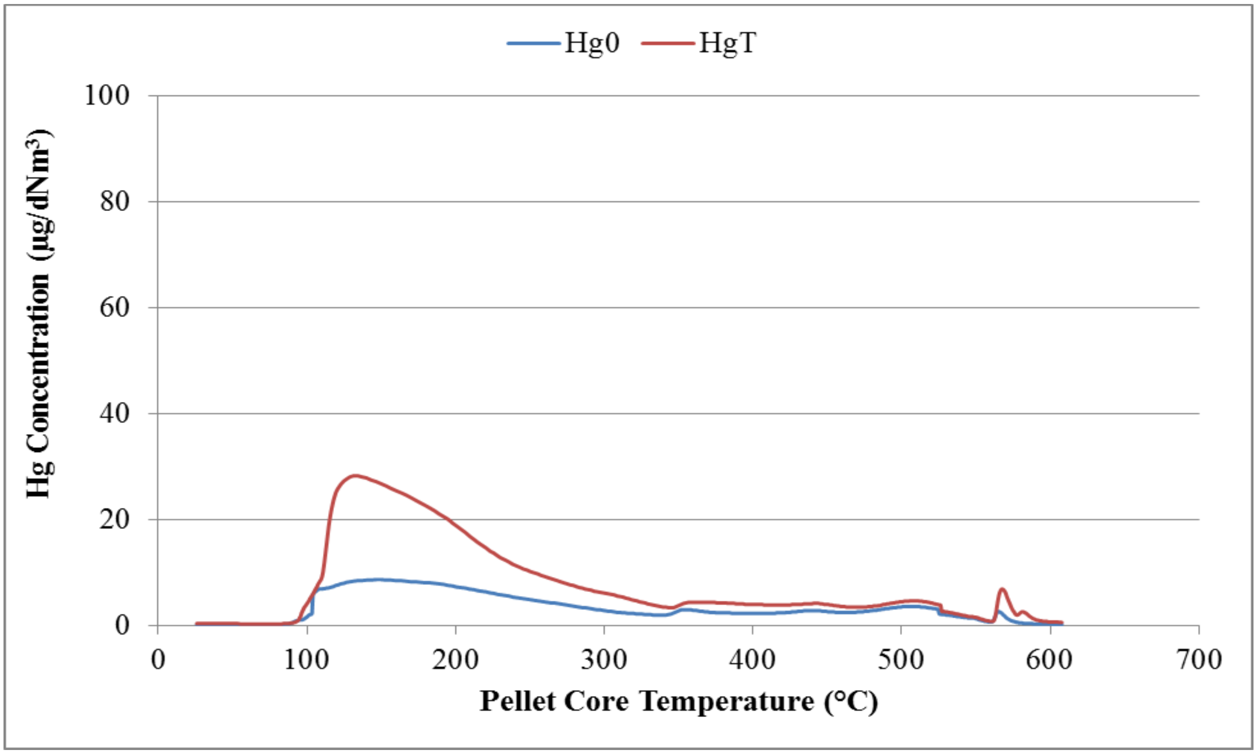

Figure 48. Mercury release profile for Arcelor Mittal first 0.5wt% loading run.

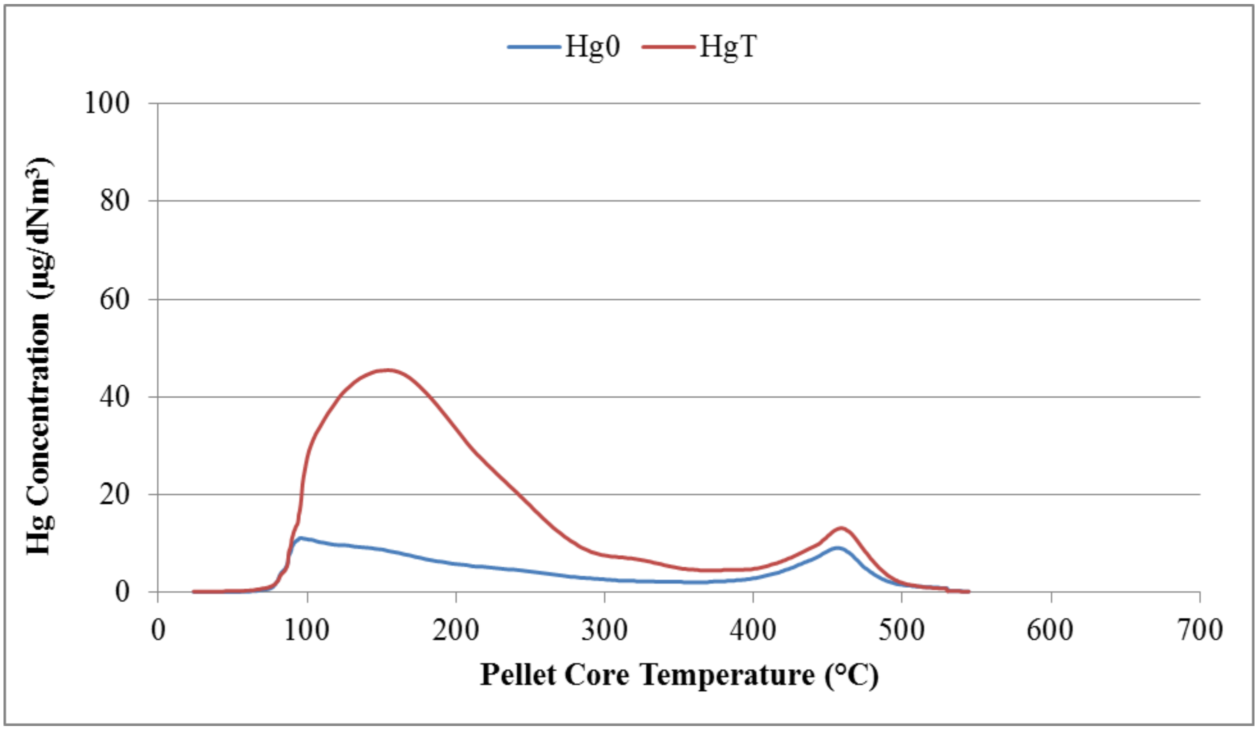

Figure 49. Mercury release profile for Arcelor Mittal second 0.5wt% loading run.

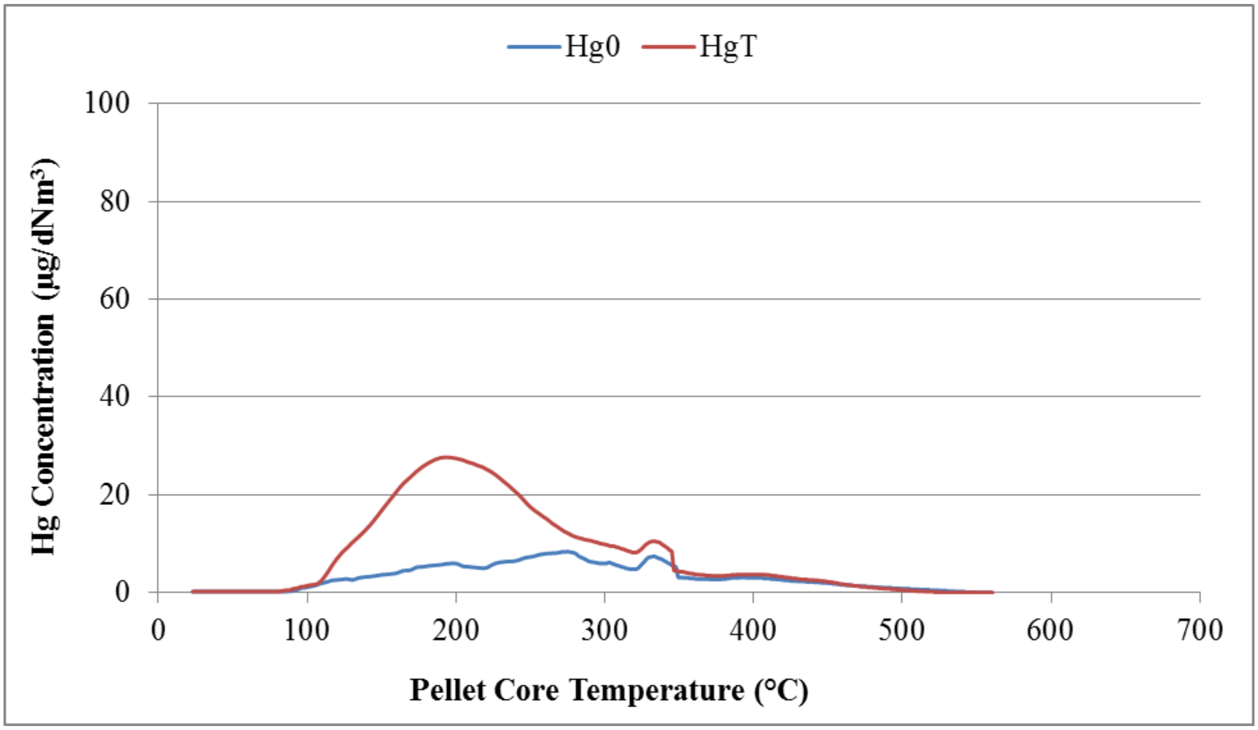

Figure 50. Mercury release profile for Arcelor Mittal third 0.5wt% loading run.

Keetac Baseline Test Results:

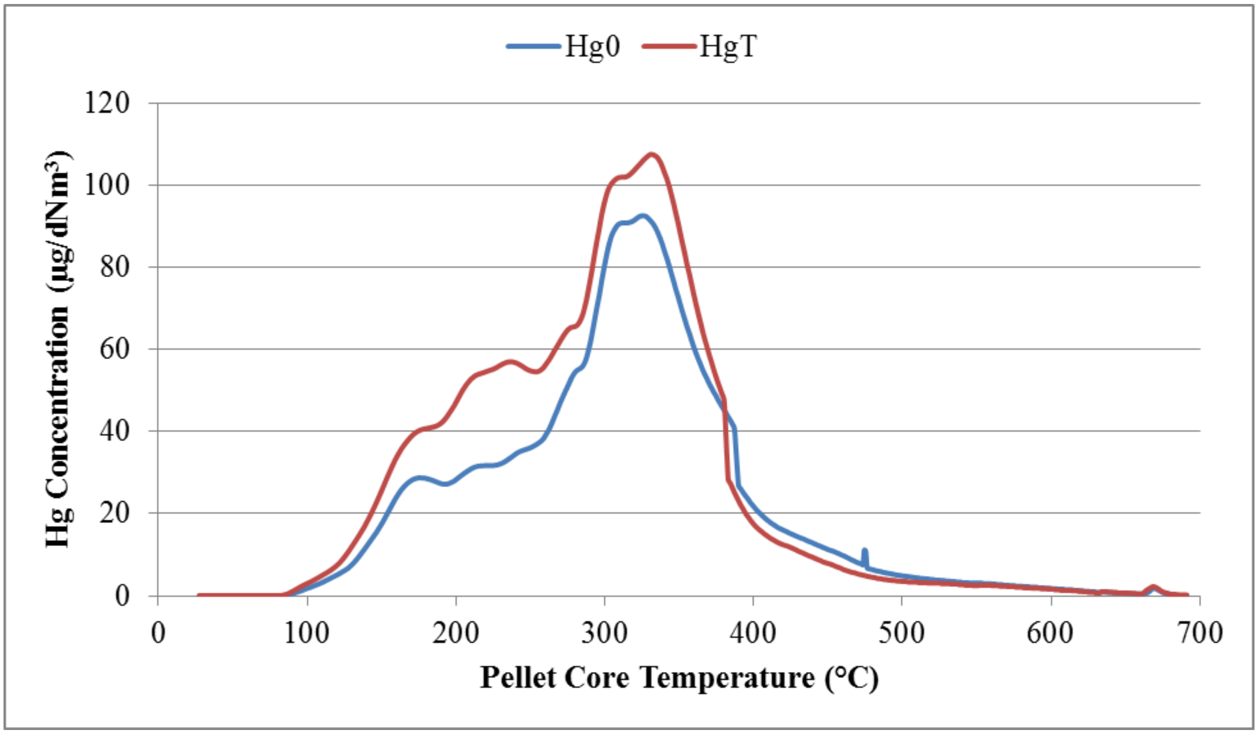

Figure 51. Mercury release profile for Keetac first baseline run.

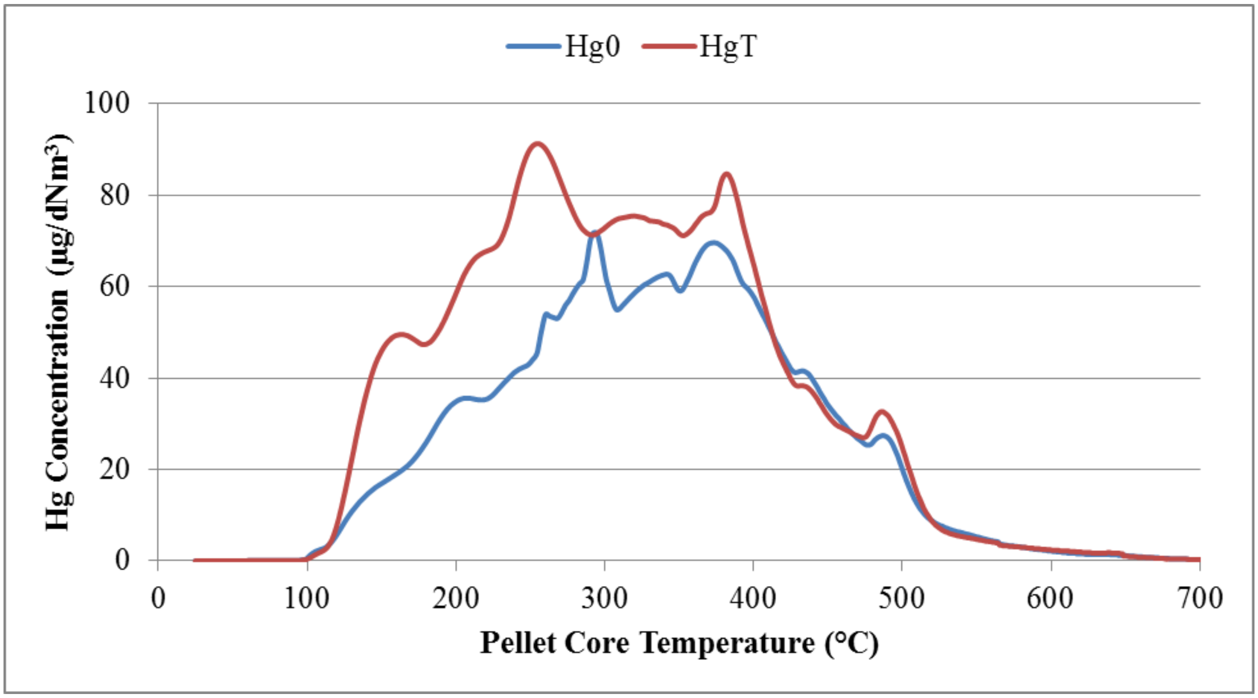

Figure 52. Mercury release profile for Keetac second baseline run.

Keetac 0.1wt% Loading Results:

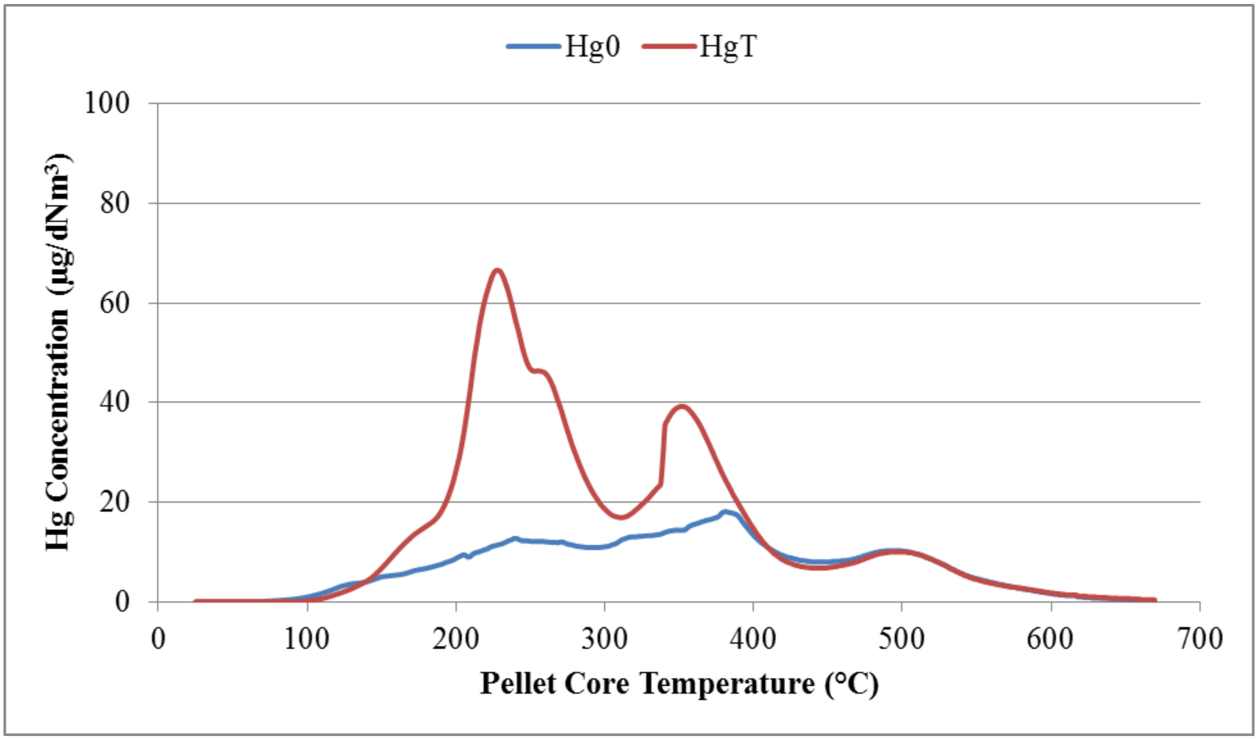

Figure 53. Mercury release profile for Keetac second 0.1wt% run.

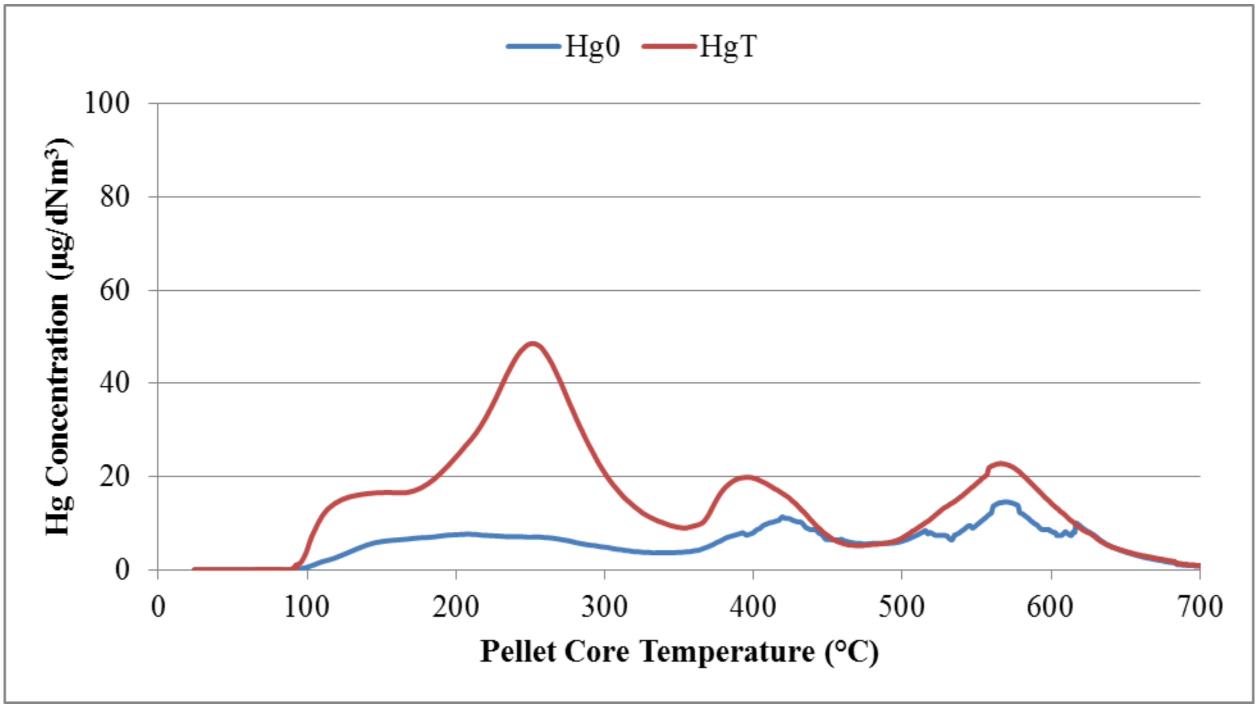

Figure 54. Mercury release profile for Keetac replicate first 0.1wt% run.

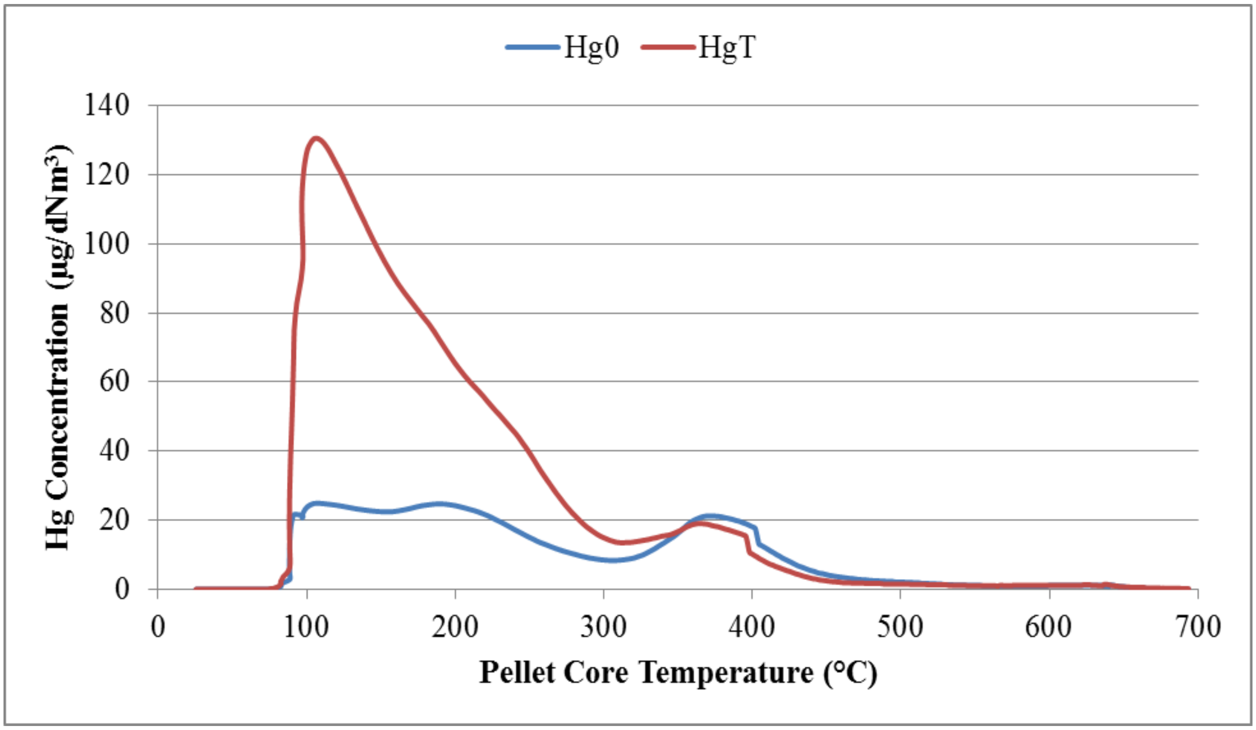

Figure 55. Mercury release profile for Keetac replicate second 0.1wt% run.

Keetac 0.5wt% Test Results:

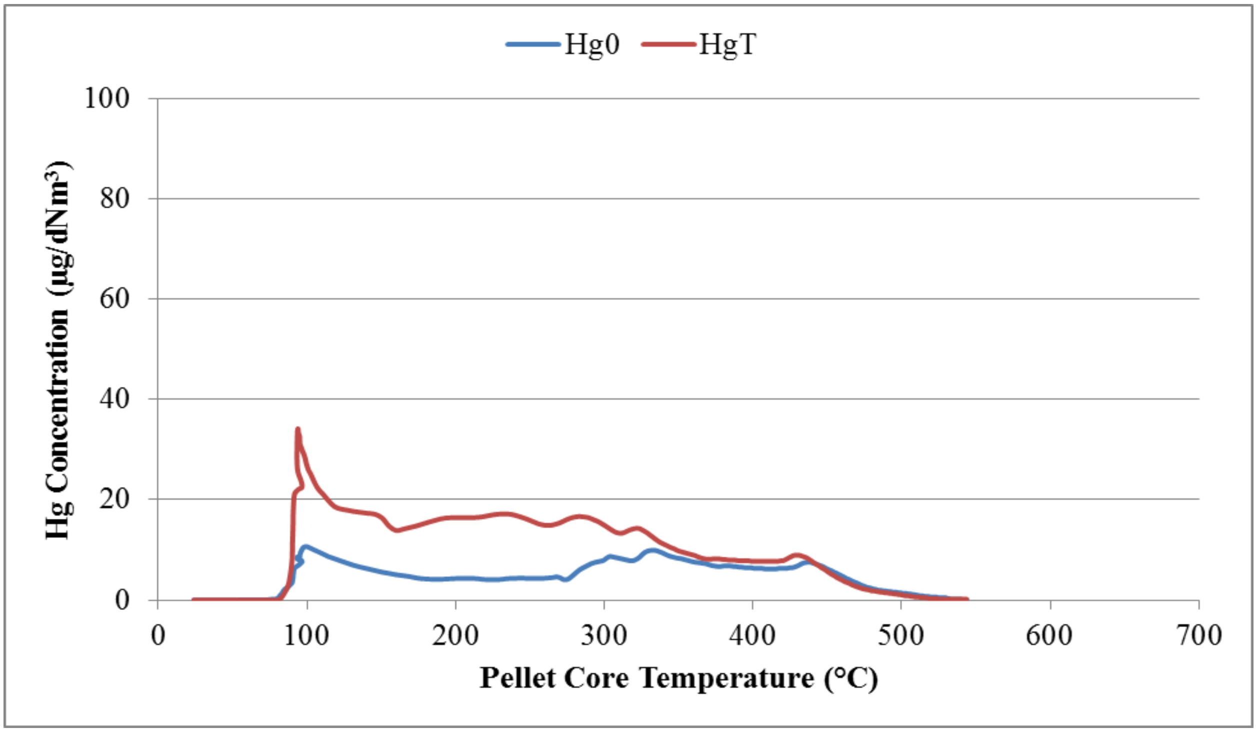

Figure 56. Mercury release profile for Keetac second 0.5wt% run.

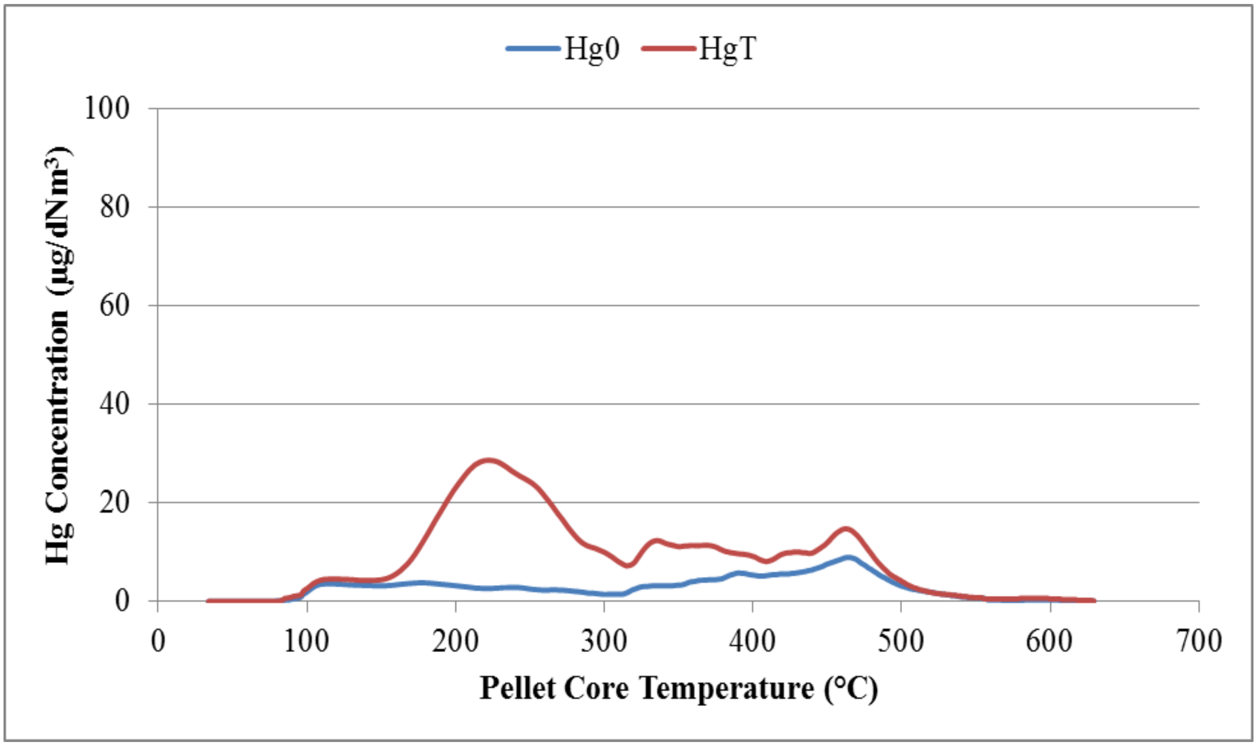

Figure 57. Mercury release profile for Keetac third 0.5wt% run.

Hibtac Standard Green Ball Baseline Test Results:

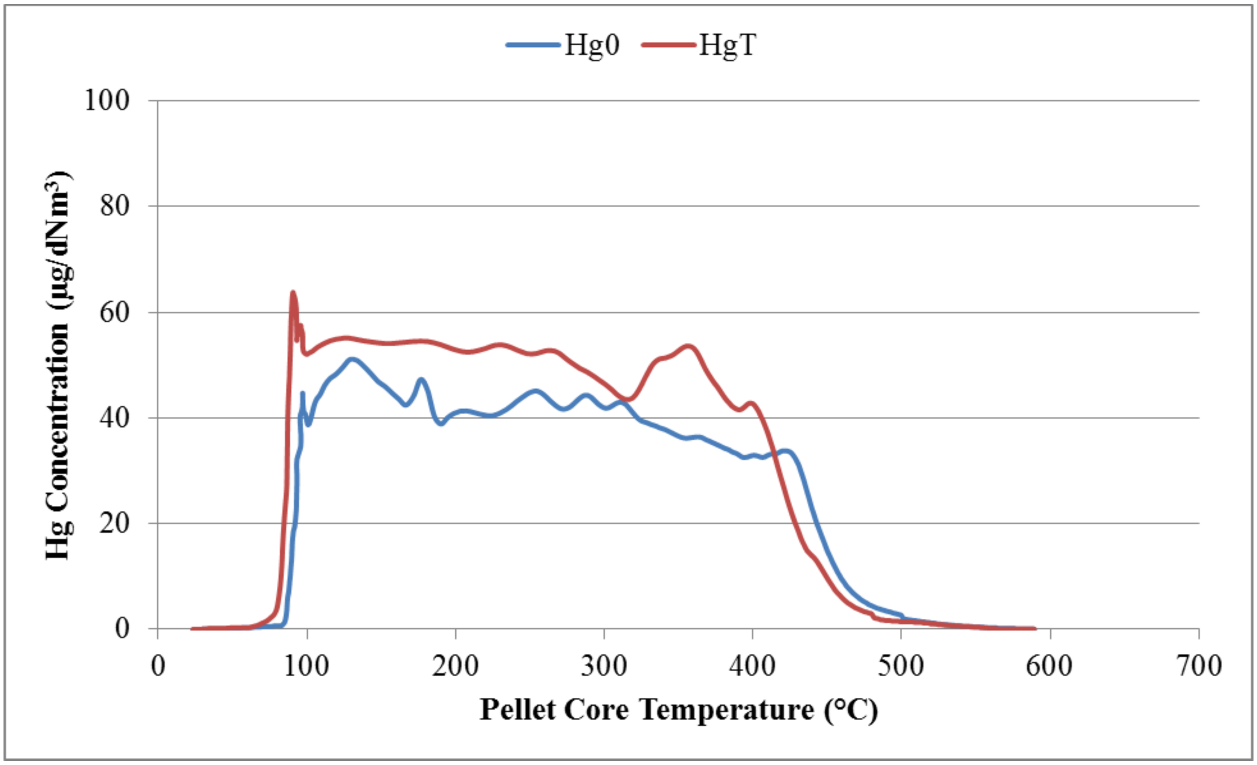

Figure 58. Mercury release profile for Hibtac standard green ball second baseline run.

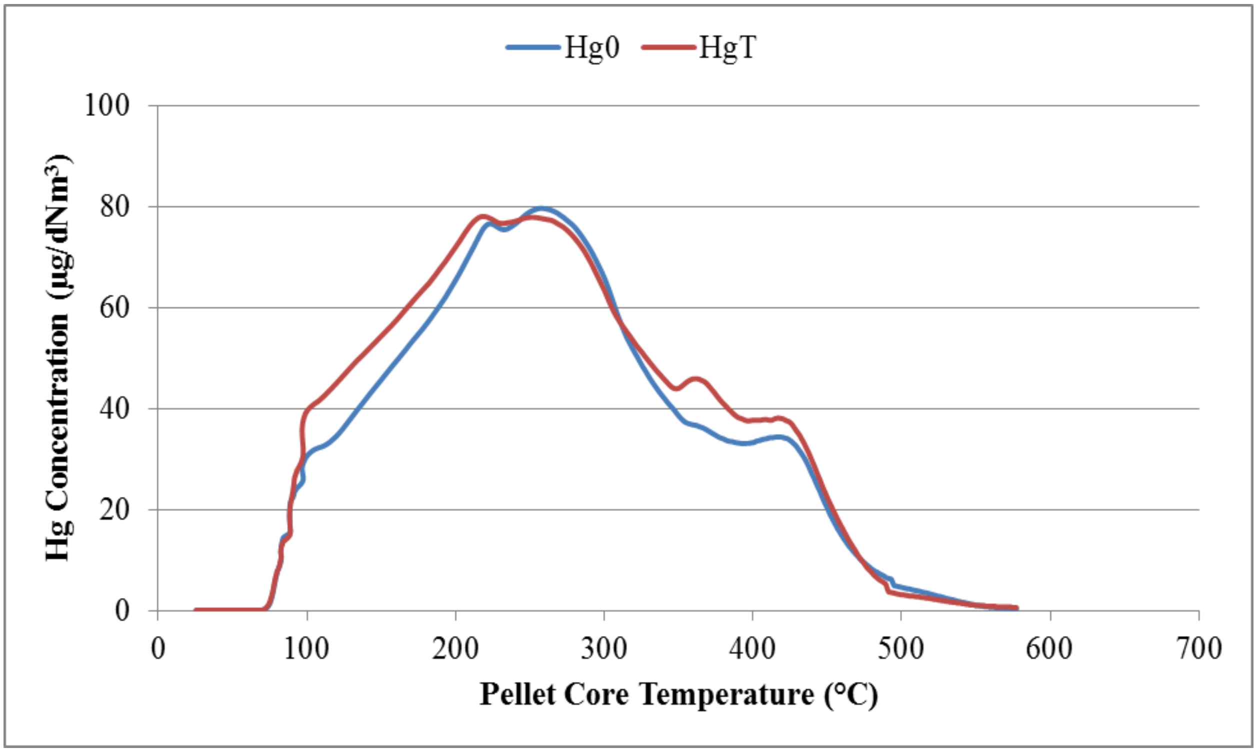

Figure 59. Mercury release profile for Hibtac standard green ball third baseline.

Hibtac Standard Green Ball 0.1wt% Loading Test Results:

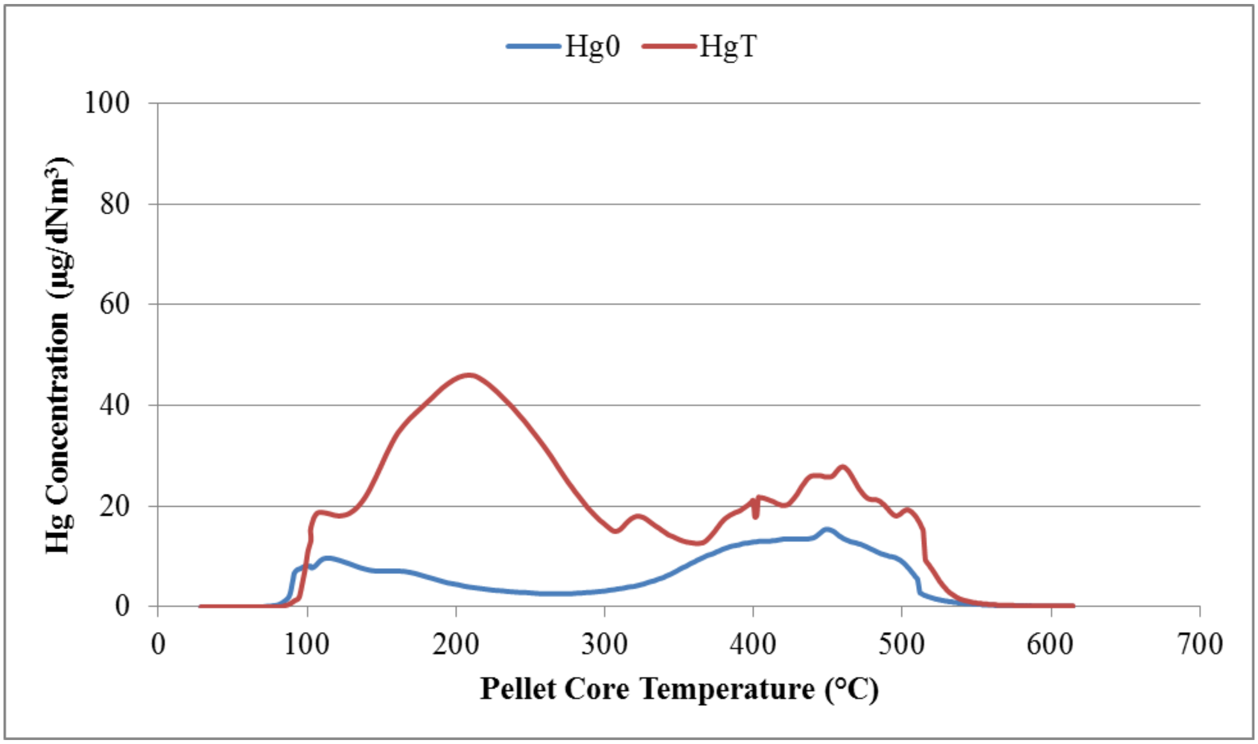

Figure 60. Mercury release profile for Hibtac standard green ball second 0.1wt% run.

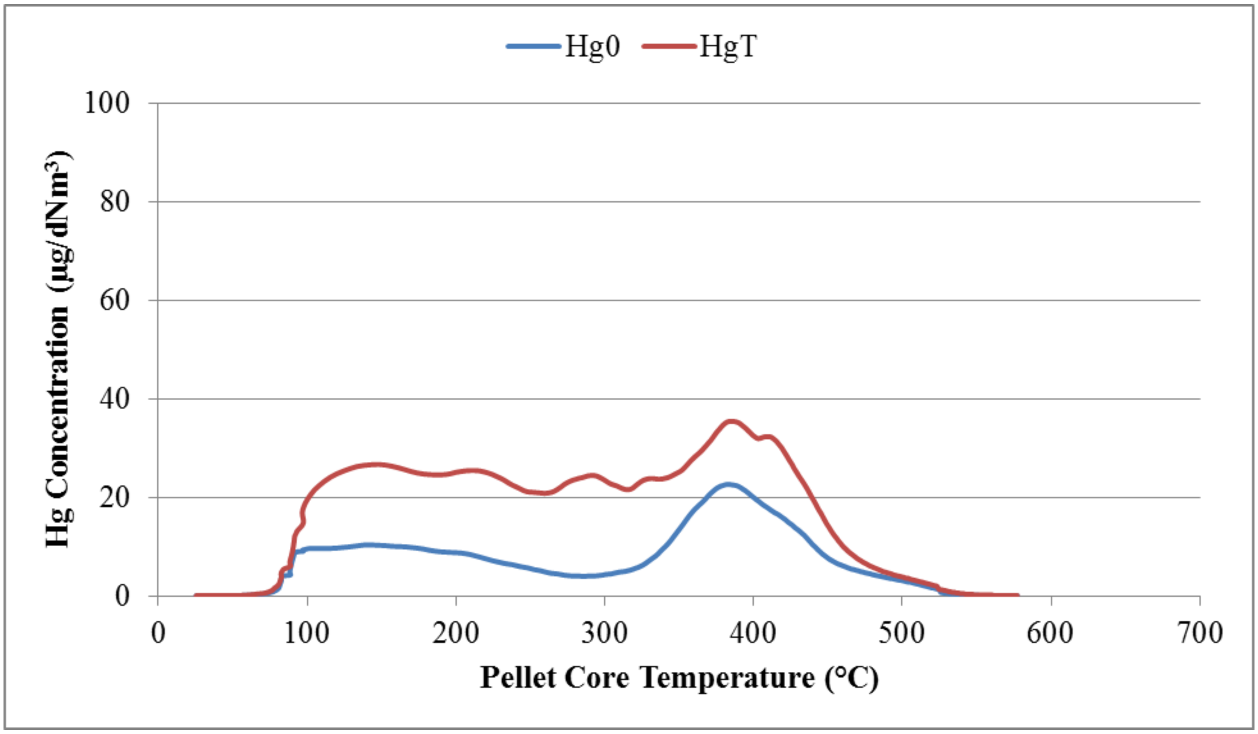

Figure 61: Mercury release profile for Hibtac standard green ball third 0.1wt% run.

Hibtac Standard Green Ball 0.5wt% Loading Test Results:

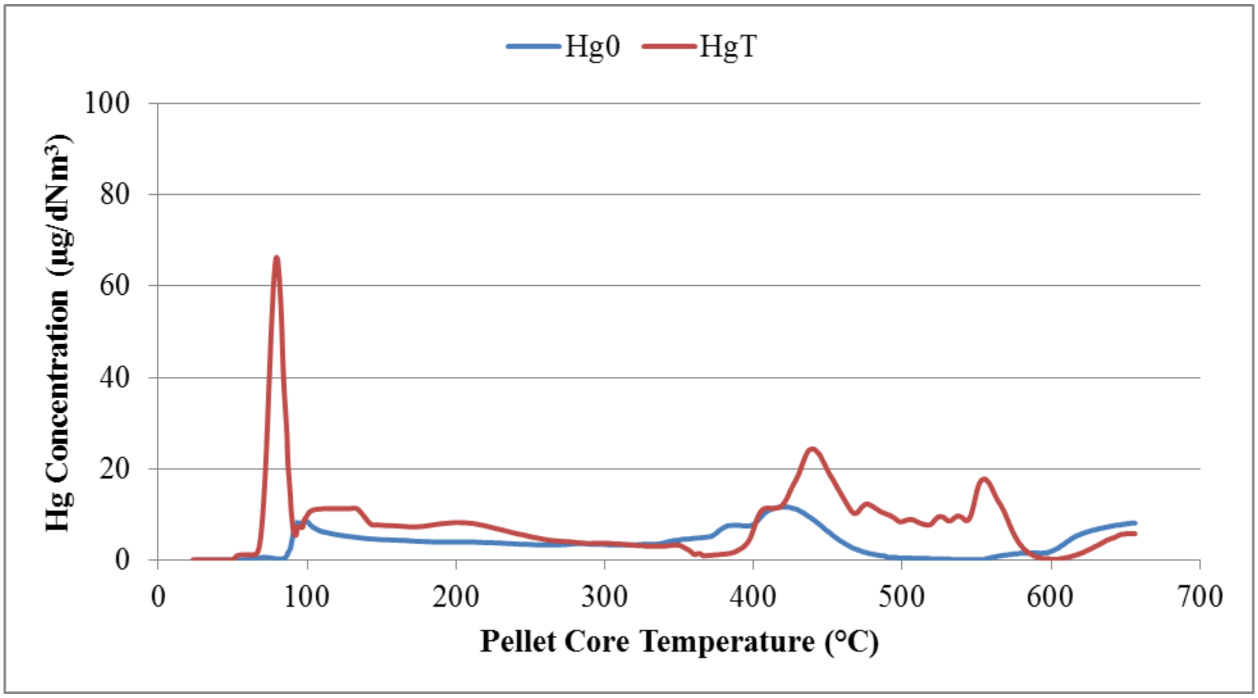

Figure 62. Mercury release profile for Hibtac standard green ball third 0.5wt% run.

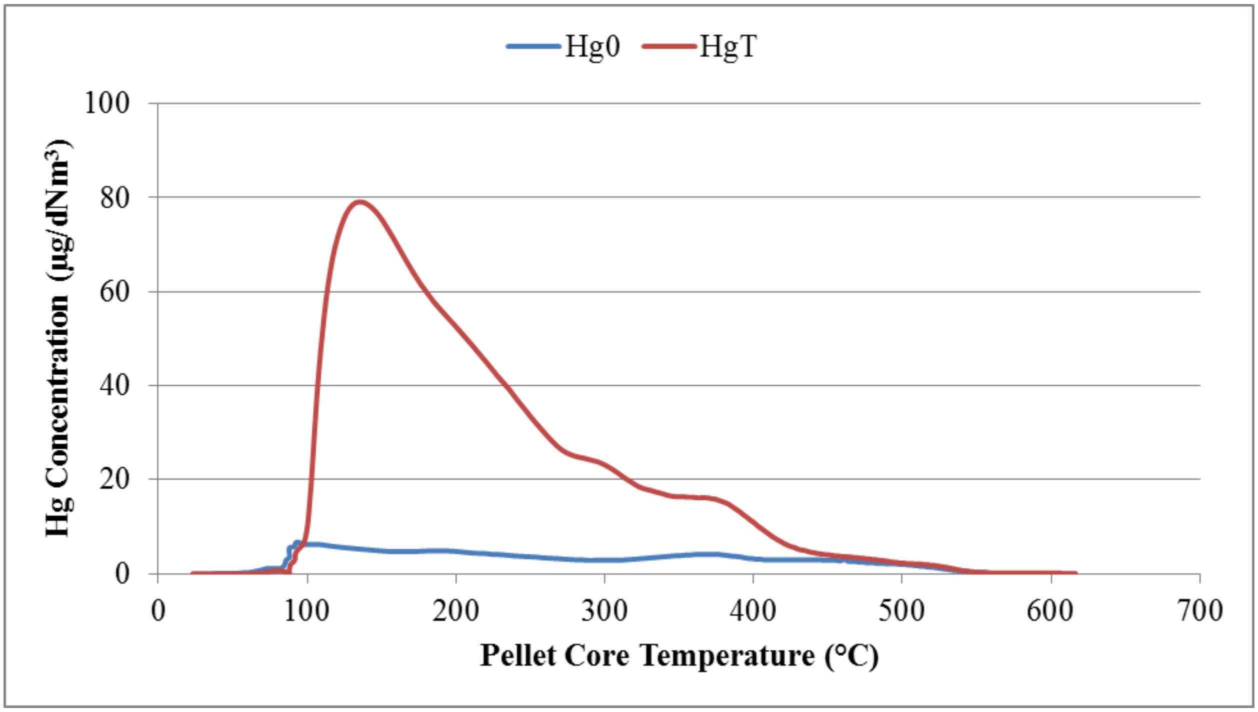

Figure 63. Mercury release profile for Hibtac standard green ball second 0.5wt% run.

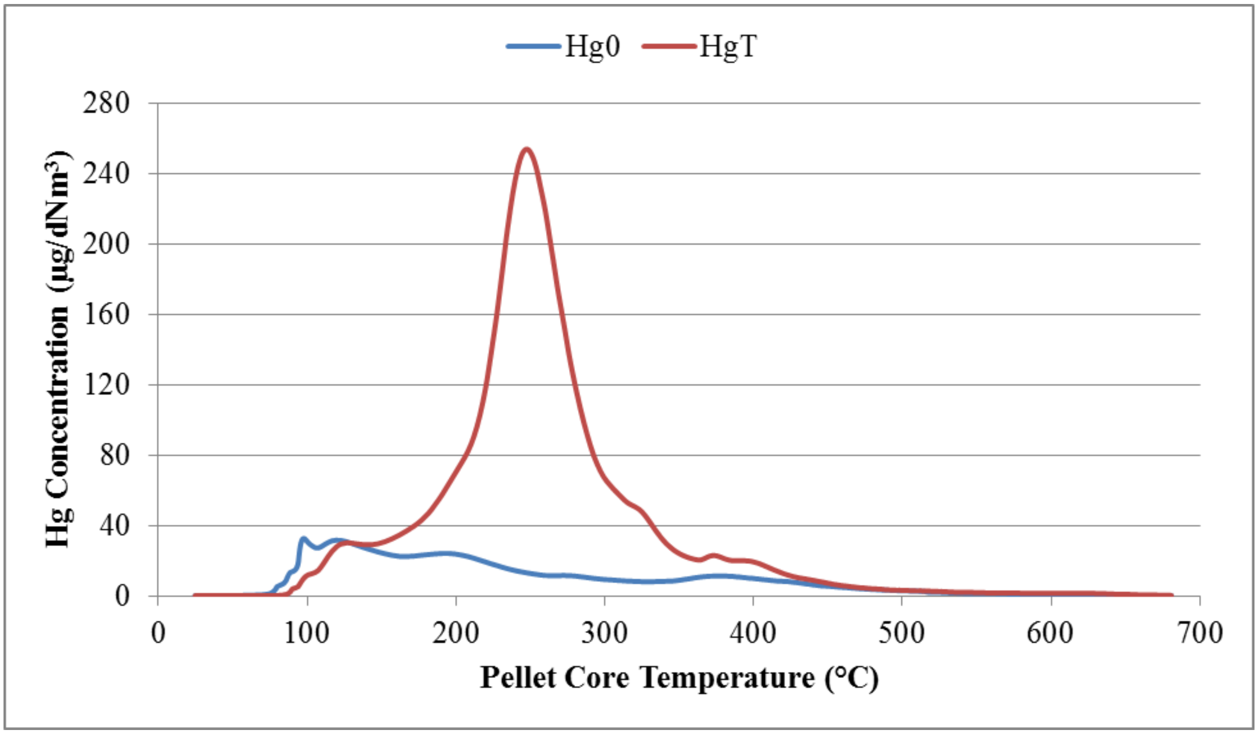

Figure 64. Mercury release profile for Hibtac standard green ball second 0.5wt% replicate run.

Hibtac High Compression Green Ball Baseline Test Results:

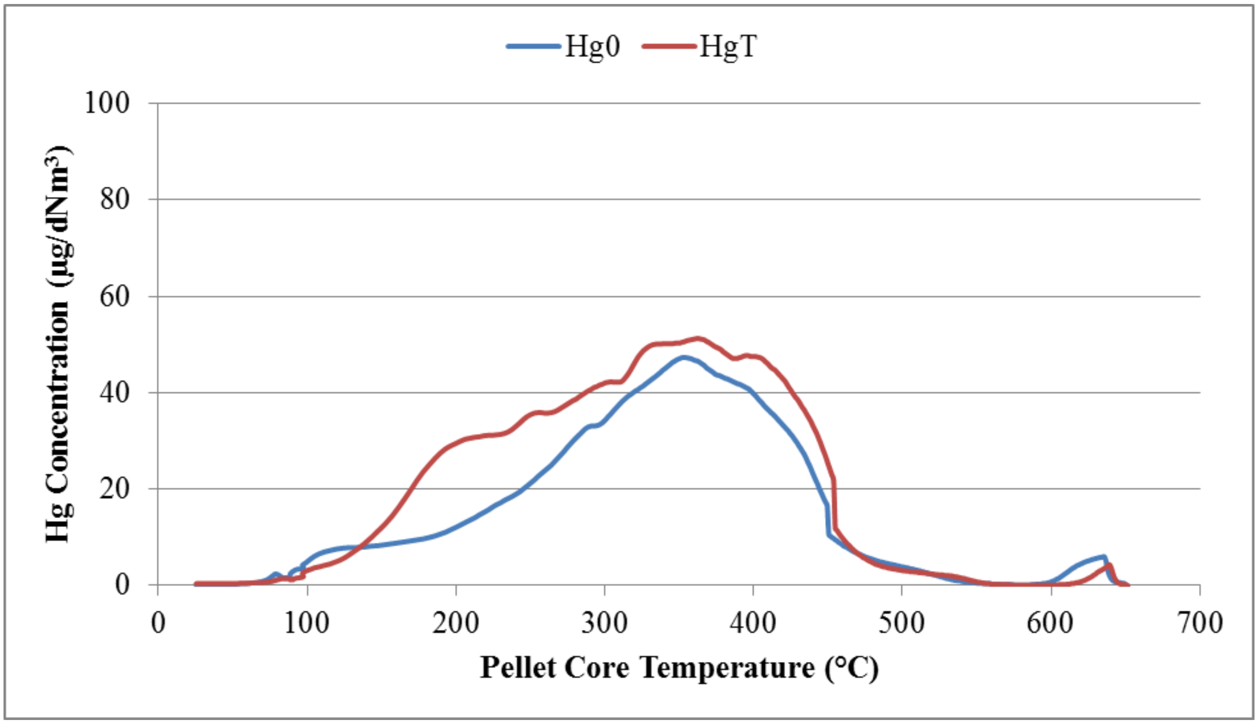

Figure 65. Mercury release profile for Hibtac high compression green ball baseline run.

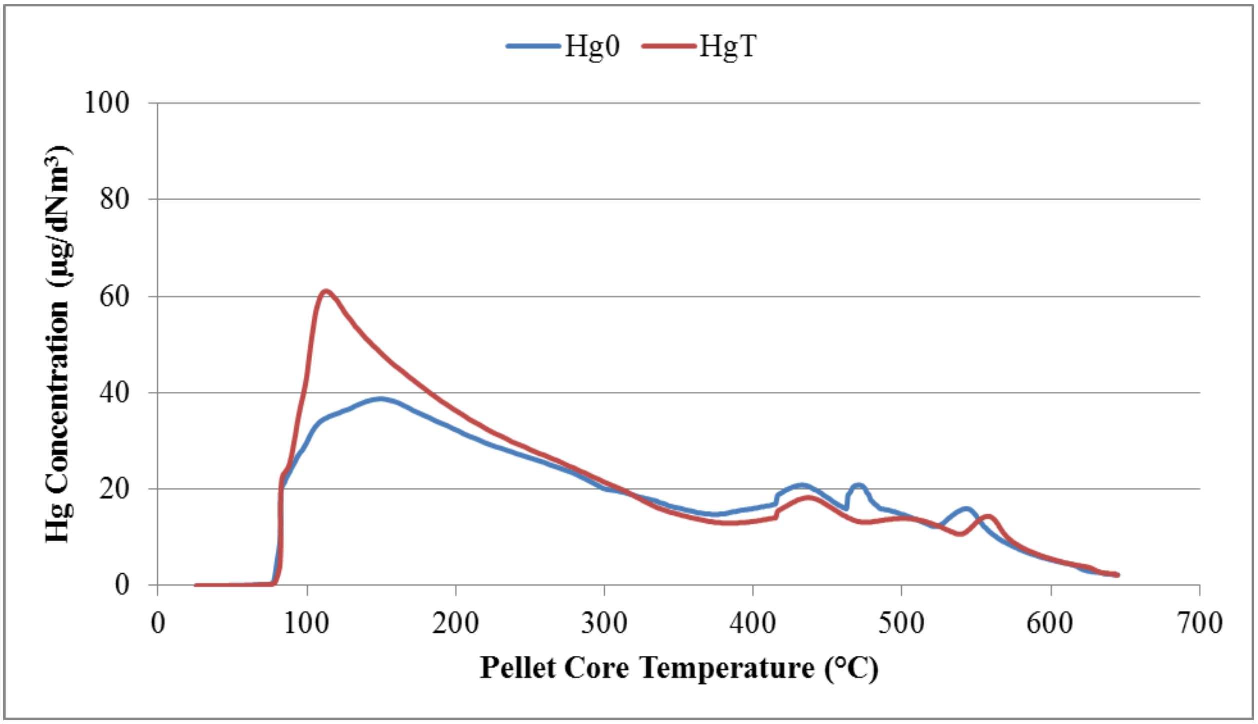

Figure 66. Mercury release profile for Hibtac high compression green ball second baseline run.

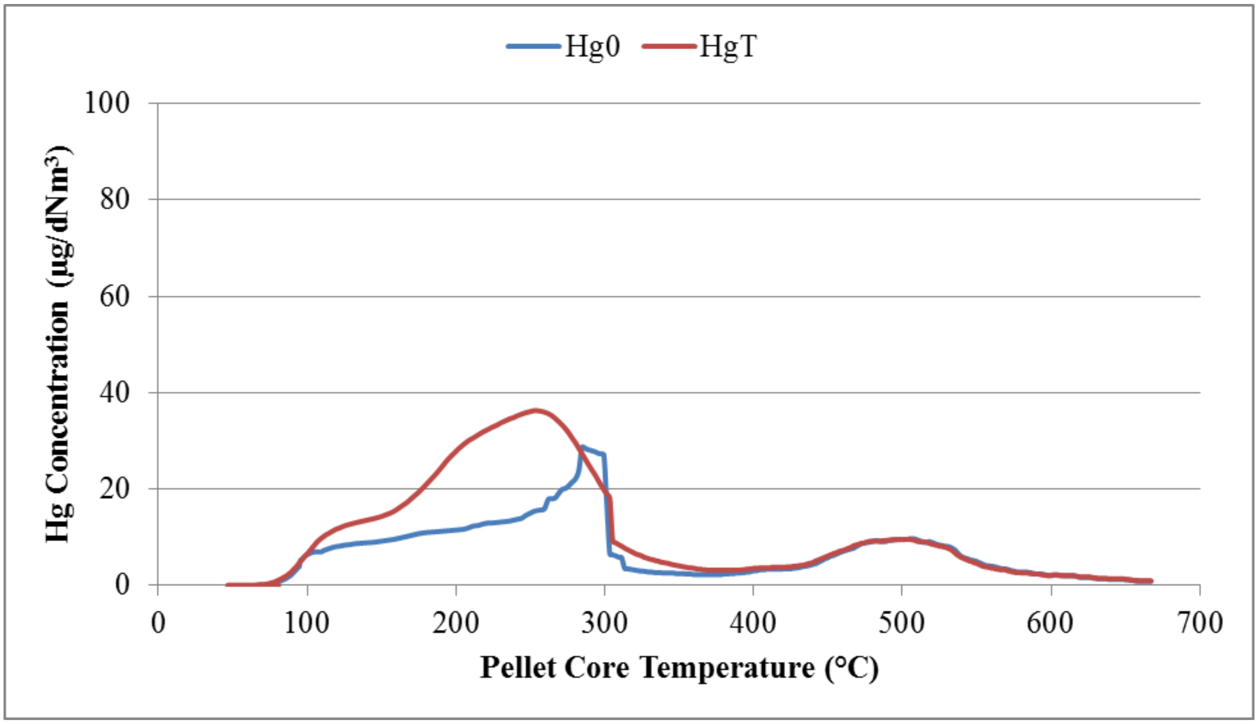

Figure 67. Mercury release profile for Hibtac compression green ball first replicate baseline run.

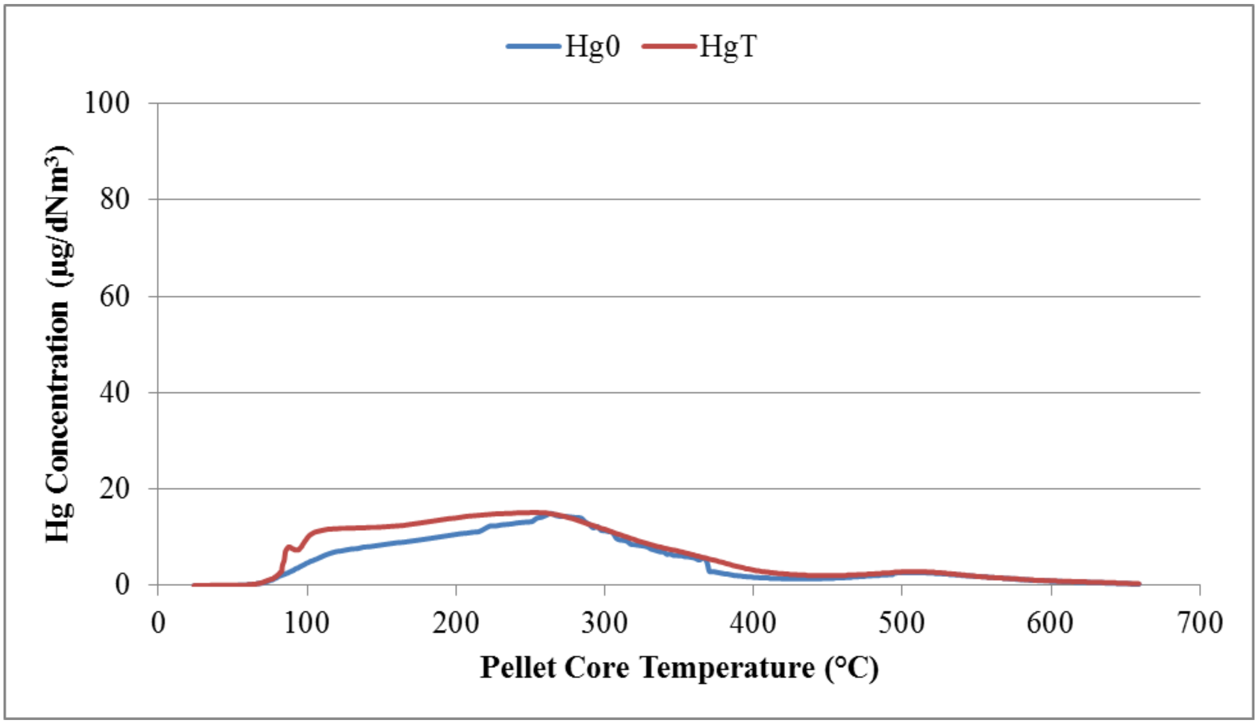

Figure 68. Mercury release profile for Hibtac compression green ball second replicate run.

Hibtac High Compression Green Ball 0.1wt% Test Results:

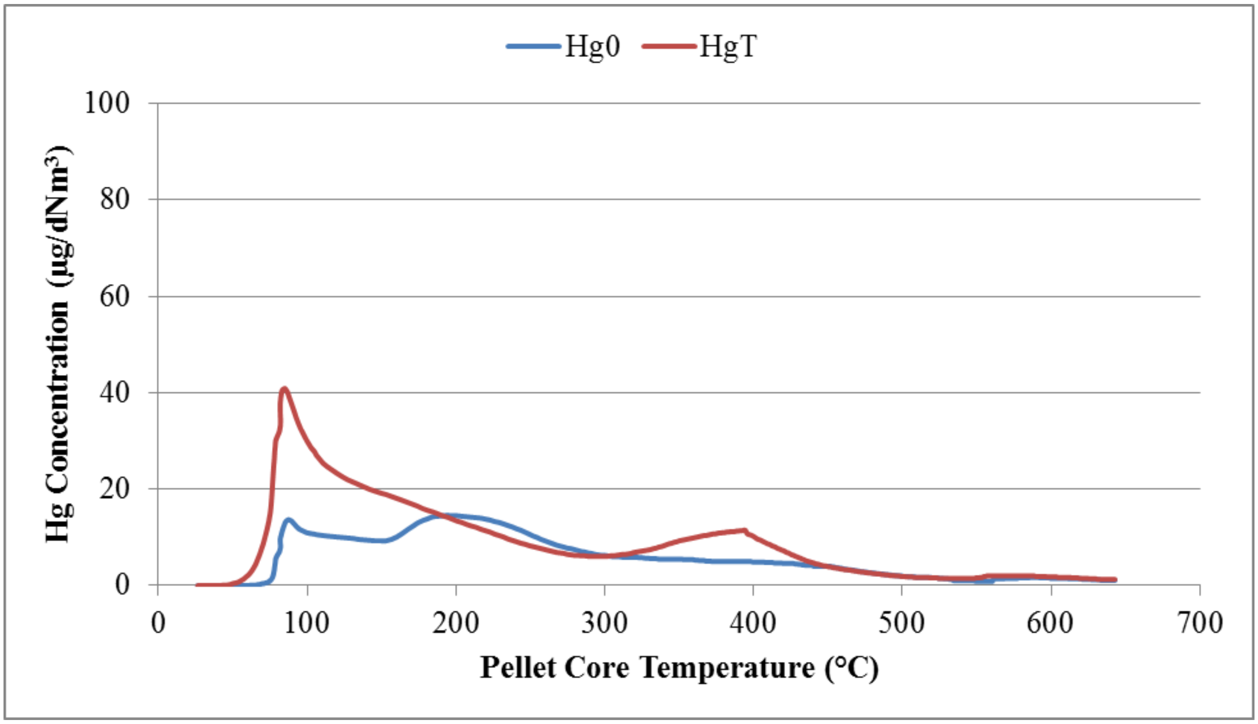

Figure 69. Mercury release profile for Hibtac compression green ball first 0.1wt% run.

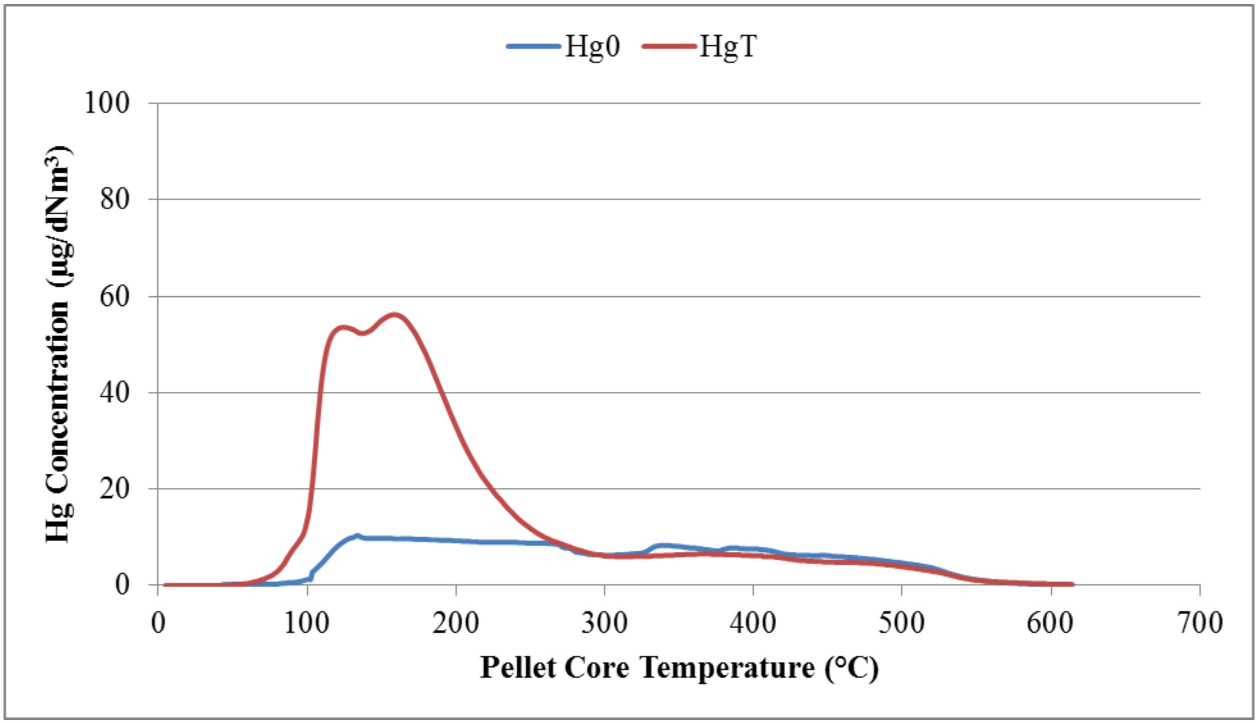

Figure 70. Mercury release profile for Hibtac compression green ball second 0.1wt% run.

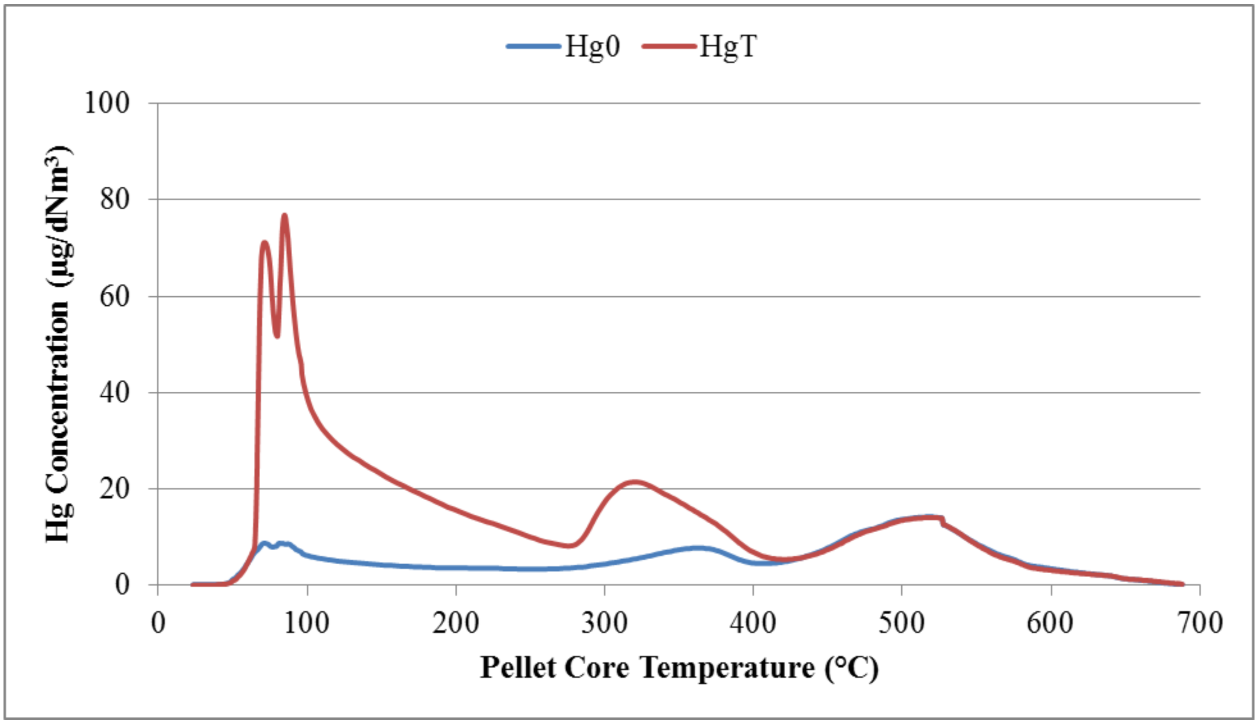

Figure 71. Mercury release profile for Hibtac compression green ball third 0.1wt% run.

Hibtac High Compression Green Ball 0.5wt% Test Results:

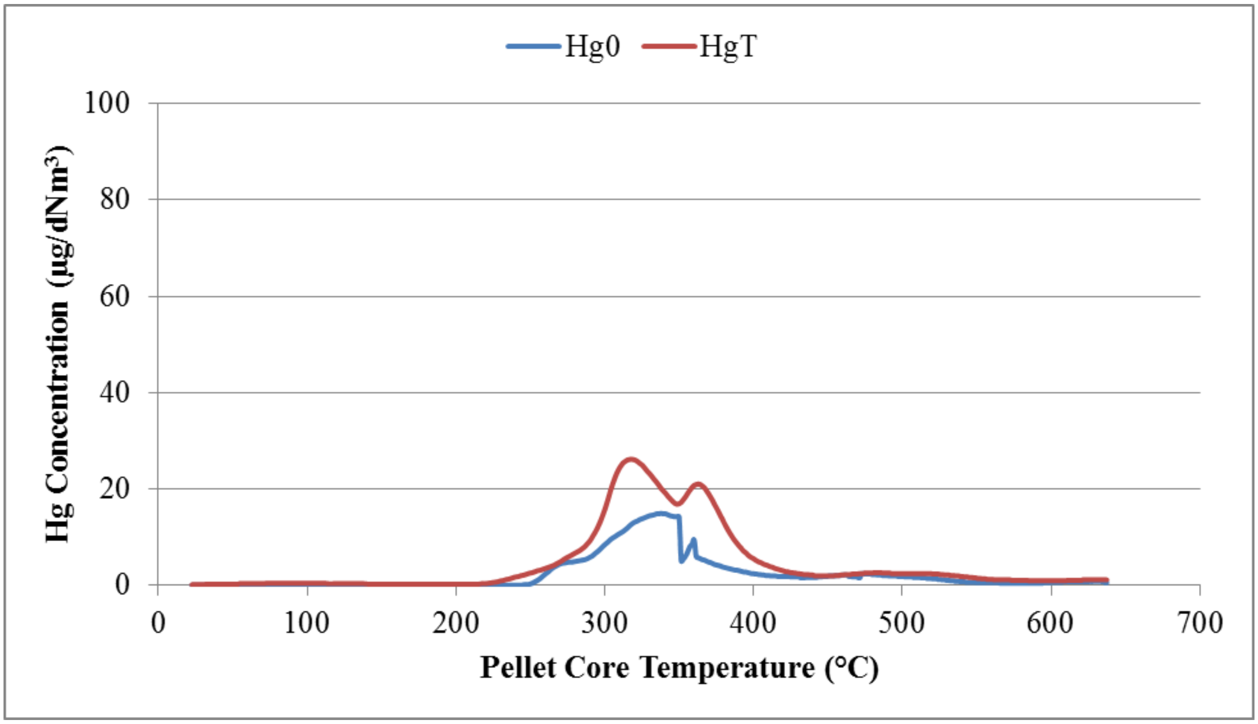

Figure 72. Mercury release profile for Hibtac compression green ball first 0.5wt% run.

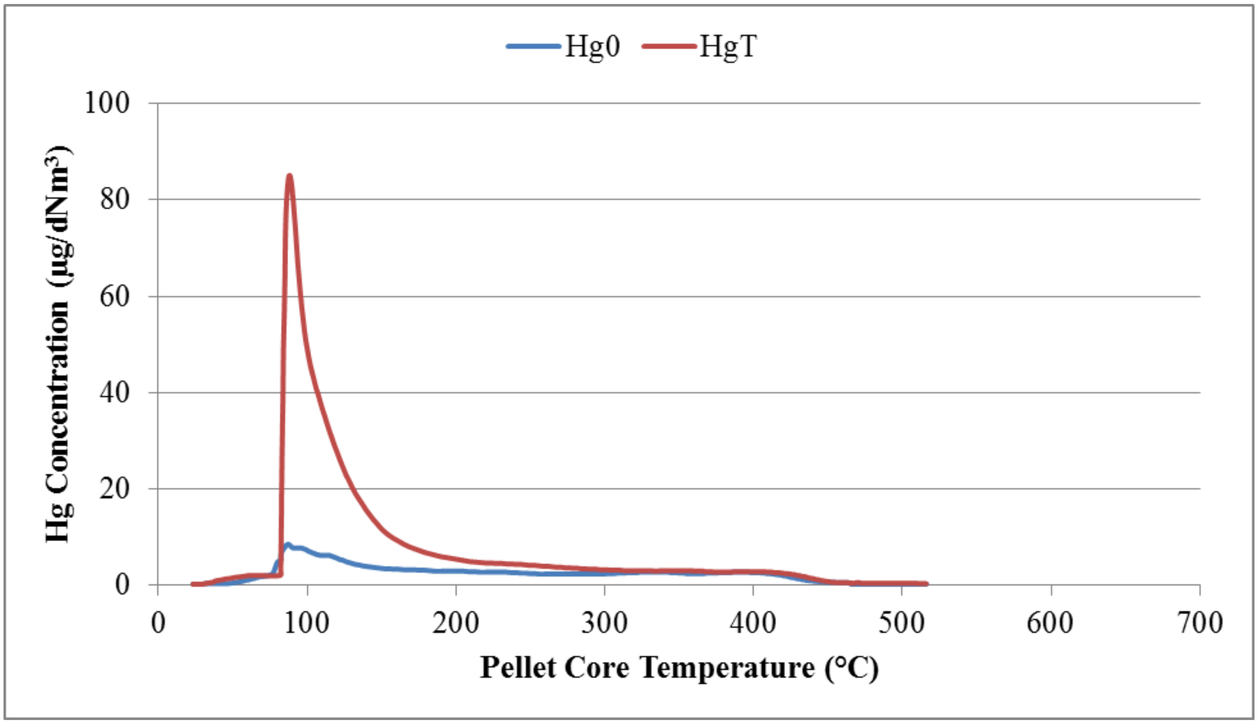

Figure 73. Mercury release profile for Hibtac compression green ball second 0.5wt% run.

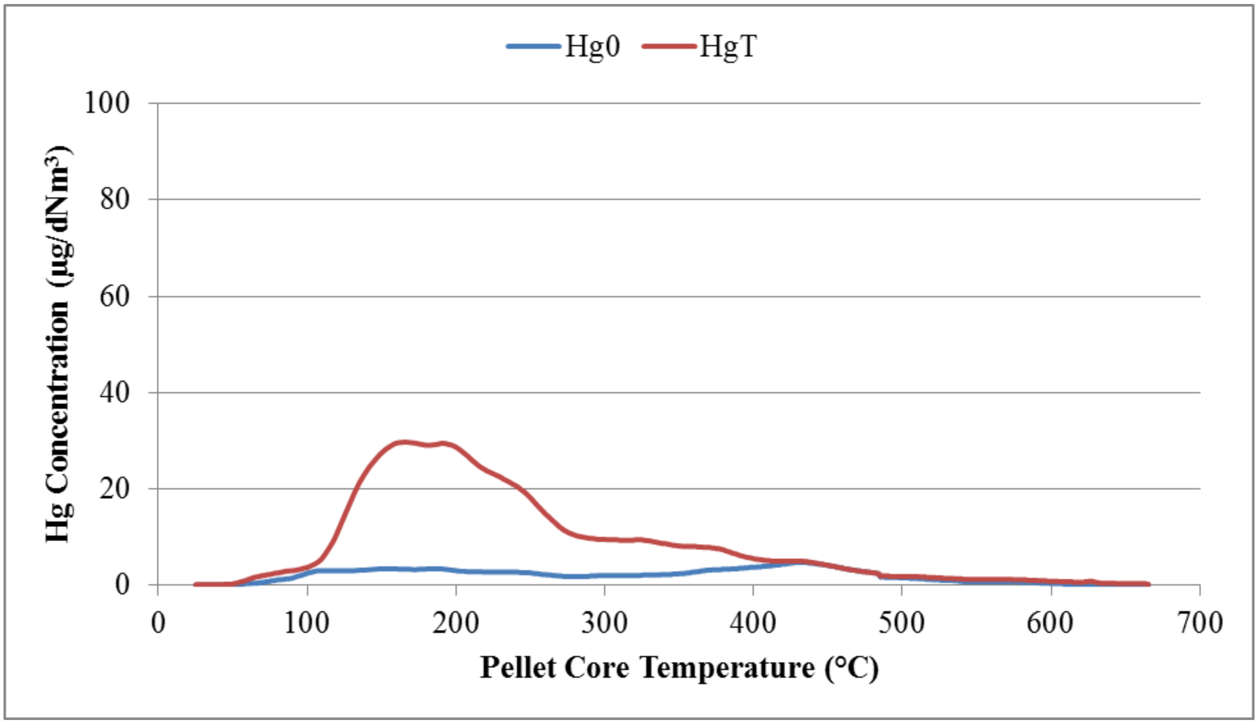

Figure 74. Mercury release profile for Hibtac compression green ball third 0.5wt% run.

Appendix B – Batch Balling Results Report

UNIVERSITY OF MINNESOTA

Duluth Campus

Coleraine Minerals Research Laboratory

Natural Resources Research Institute

Box 188
One Gayley Avenue
Coleraine, Minnesota 55722

218-245-4201
Fax: 218-245-4219

July 6, 2012

Nicholas Lentz, Ph.D.
Associate Director for Energy Technology Applications
Shuchita Patwardhan
Graduate Research Assistant

Institute for Energy Studies
The University of North Dakota
243 Centennial Drive Stop 8153
Upson II Room 366L
Grand Forks, ND 58202
(701)-777-2684

RE: Batch Balling Tests with University of North Dakota Carbon Additive

Introduction

A series of batch balling tests were conducted from 6/25 – 6/28/2012 to evaluate a carbon based additive supplied by the University of North Dakota (UND) to green taconite agglomerates and compare them to a standard baseline to determine an influence on the green ball properties. The testing sequence consisted of three tests and one repeat (4 tests total) for each of six Taconite Mining Operations in Northern Minnesota. The three tests consisted of a low and high level carbon additive rate of 0.1% and 0.5% and a baseline with 0.0% additive. The repeat test appears to be random and was supplied by UND. The basis for each of the six operations, Arcelor-Mittal Minorca, U.S. Steel Keewatin Taconite, Hibbing Taconite, U.S. Steel Minntac and United Taconite was determined from current plant operations and prior batch balling testing conducted at the Coleraine Minerals Research Laboratory.

Discussion

Batch balling tests were conducted to compare the physical quality of green balls prepared with the concentrates and additives described in the attached table. The raw materials were all collected fresh from the respective plants in the weeks prior to testing and were used “as received” except for the Minntac which sent a filter cake that required filtering prior to use. Low level fluxstone addition was done as necessary in blended in a dry state to ensure proper green ball chemistry representative of the specific plant operation.

Batch Balling Procedure:

The mixes are prepared on a dry weight basis of 3000 g iron ore concentrate including the limestone/fluxstone addition. Binders are added in excess of the concentrate blends on the basis of lbs./Dry Long Ton (DLT) concentrate. The binder addition rates used in this study were used within the acceptable guidelines of typical plant operations. The binders (bentonite or organic) were added with the carbon additive. The carbon sorbent was added in several “small portions” sprinkled into the concentrate and blended by hand in a lab mixing bowl. This technique has been compared to low intensity mixing, typical of most operations, with no significant variance. Once the mixes are blended, they are pushed through a laboratory shredder to eliminate any micro agglomerates to prepare them for agglomeration in the balling tire. Figure 1 shows the batch balling test equipment and arrangement, consisting of a shredder and balling tire.

Figure 1. Batch balling test equipment and arrangement

The concentrate blend is initially added to the balling tire in small amounts to produce “seed” balls. Seed balls are screened at -3Mesh +4Mesh. Each plant operation requires a specified amount of seeds (typically between 170 and 250g) to duplicate plant green ball quality. The green balls for testing are then grown from the seeds by slowly adding concentrate to build them up to target size. The procedure requires the addition of the remaining concentrate blend over a period of 3 minutes, followed by a 1 minute “roll”. Target sized green balls are -1/2” + 3/8”.
Analysis:
The green balls are screened to obtain a size distribution used for comparative purposes and for measuring relative growth rate. It should be noted that this may or may not be representative of actual plant green balls size distribution. A sample is placed in a drying oven to determine moisture content. Separate samples of the green balls are measured for 18” wet drop number. Once green the balls are dried, the moisture is calculated and the dried balls are then measured for dry compressive strength.

Results / Conclusions

Results of these tests are provided in the attached table. Green ball quality is a key parameter in the operation of an induration furnace from the standpoint of bed permeability, airflow, and dust generation. The data shows that the addition of the UND carbon additive at both low and high level addition has no significant effect on green ball moisture or wet drop number when compared to a baseline standard. In addition, the additive shows no significant influence on dry compression strength of green balls prepared with fluxstone addition or the standard green ball prepared with the organic binder for United Taconite. The standard green balls prepared for Hibbing Taconite (with a very low level limestone addition) and Keewatin taconite (no limestone) show a slight decrease in the dry compression at the higher dosage rate of 0.5%. It should be noted that these two operations also have much coarser particle size distribution due to their relative location on the Minnesota Iron Range and the transition in the silica liberation characteristics of the ore body. In some cases, the data also indicates the relative green ball size distribution is slightly larger (+1/2” size fraction) with the higher additive rate, however this should be further studied as it is not fully verified by the data.

Richard Kiesel
Deputy Director
High Temperature Processing and Bio-Energy Conversion
University of Minnesota Duluth
Natural Resources Research Institute
Coleraine Minerals Research lab
PO Box 188
One Gayley Ave.
Coleraine, MN 55722
Ph: 218-245-4207
Fax: 218-245-4219
e-mail: rkiesel@nrri.umn.edu

Table 1: Results of Batch Balling Tests

						Green Ball Quality			Green Ball Sizing, %		
Test #	Iron Ore Concentrate	Description	Binder	Additive (s)	UND Carbon Additive, %	Moist, %	18" Drop	Dry Comp	+1/2"	-1/2" +7/16"	-7/16" +3/8"
B12576	Arcelor Mittal	Fluxed	Bentonite	Limestone-Dolomite	0.0	9.8	7.5	7.8	0.5	44.0	55.6
B12577	Arcelor Mittal	Fluxed	Bentonite	Limestone-Dolomite	0.1	9.9	8.2	9.0	1.1	48.4	50.5
B12578	Arcelor Mittal	Fluxed	Bentonite	Limestone-Dolomite	0.5	9.8	7.2	7.1	1.8	55.8	42.4
B12579	Arcelor Mittal	Fluxed	Bentonite	Limestone-Dolomite	0.1	9.7	7.1	7.9	7.3	64.2	28.5
Std Deviation						0.1	0.5	0.8			
B12580	Keetac	Std	Bentonite	--	0.0	9.4	4.8	6.8	11.7	49.2	39.0
B12581	Keetac	Std	Bentonite	--	0.1	9.5	4.9	5.6	6.8	46.4	46.8
B12582	Keetac	Std	Bentonite	--	0.5	9.2	4.5	3.1	14.8	43.2	42.0
B12583	Keetac	Std	Bentonite	--	0.1	9.5	5.7	5.7	7.7	52.2	40.1
Std Deviation						0.1	0.5	1.6			
B12584	Hibtac	Std Pellet	Bentonite	Low Level Limestone	0.0	9.7	6.5	8.8	1.8	46.9	51.2
B12585	Hibtac	Std Pellet	Bentonite	Low Level Limestone	0.1	9.6	6.3	8.4	3.5	51.3	45.2
B12586	Hibtac	Std Pellet	Bentonite	Low Level Limestone	0.5	9.5	6.2	3.9	10.2	47.1	42.7
B12587	Hibtac	Std Pellet	Bentonite	Low Level Limestone	0.5	9.6	6.0	4.3	4.6	46.4	49.0
Std Deviation						0.1	0.2	2.6			
B12588	Hibtac	High Comp	Bentonite	Low Level Limestone	0.0	9.6	6.8	7.2	2.8	52.4	44.8
B12589	Hibtac	High Comp	Bentonite	Low Level Limestone	0.1	9.7	6.1	9.0	1.7	35.0	63.3
B12590	Hibtac	High Comp	Bentonite	Low Level Limestone	0.5	9.6	6.3	7.9	6.1	57.1	36.7
B12591	Hibtac	High Comp	Bentonite	Low Level Limestone	0.0	9.5	6.5	8.8	2.9	48.6	48.5
Std Deviation						0.1	0.3	0.8			
B12592	Minntac	Fluxed	Bentonite	Limestone-Dolomite	0.0	9.5	6.8	8.6	0.3	33.6	66.0
B12593	Minntac	Fluxed	Bentonite	Limestone-Dolomite	0.1	9.6	6.5	8.1	0.7	47.2	52.1
B12594	Minntac	Fluxed	Bentonite	Limestone-Dolomite	0.5	9.2	5.9	6.0	3.3	54.7	42.0
B12595	Minntac	Fluxed	Bentonite	Limestone-Dolomite	0.0	9.2	6.2	8.8	0.5	37.4	62.1
Std Deviation						0.2	0.4	1.3			
B12596	Utac	Std	Organic	Low Level Limestone	0.0	9.9	5.0	2.1	25.2	40.1	34.6
B12597	Utac	Std	Organic	Low Level Limestone	0.1	10.1	5.5	2.8	7.6	50.5	41.9
B12598	Utac	Std	Organic	Low Level Limestone	0.5	10.2	5.9	3.1	11.4	49.2	39.3
B12599	Utac	Std	Organic	Low Level Limestone	0.5	9.7	5.5	2.6	12.1	39.5	48.4
Std Deviation						0.2	0.4	0.4			

Appendix C – Data Quality Assessment Worksheet

1) **Method Description/Key Parameters:**

   a) Test results from these studies would be most applicable for US Steel's Minnesota Taconite and Keewatin Taconite; Arcelor Mittal and Hibbing Taconite. Testing consists of bench scale experiments performed on green balls obtained from all five taconite facilities, with the four facilities listed above showing best results. United Taconite oxidation results were lower than for other facilities.

   b) Mercury oxidation is determined by calculating the difference between the total mercury (Hg^T) and elemental mercury (Hg^0) release during bench testing of green balls. Oxidized mercury tends to be captured by taconite wet scrubber systems, so the percent mercury oxidation is used as an estimate of the percent mercury reduction. Full-scale testing of the technology would be necessary to determine the actual reduction potential of the technology.

   - Oxidation formula:

$$\% \text{ Hg Oxidation} = \frac{\{\text{Hg}^T - \text{Hg}^0\}}{\text{Hg}^T} * 100 \quad [1]$$

   Where,

     - Hg^T is the total mercury emission during the test run.
     - Hg^0 is the total elemental mercury emission during the test run. Hg^T and Hg^0 are measured using a Horiba DM-6B Cold Vapor Atomic Absorption Spectroscopy CMM.

   - Sample calculation using Minntac 0.1wt% results:

     - Hg^T = Average total mercury concentration = 7.2 ng Hg/g GB
     - Hg^0 = Average elemental mercury concentration = 2.7 ng Hg/g GB

$$\% \text{ Hg Oxidation} = \frac{\{7.2-2.7\}*100}{7.2} = \underline{62.9\%}$$

c) The mercury reduction potential of the technology is determined using equation 2 below.

- Equation 2:

$$\text{Reduction Potential} = \frac{\text{Hg}[2] - \text{Hg}[1]}{100 - \text{Hg}[1]} * 100 \qquad [2]$$

Where,

- Hg[1] is the average mercury oxidation obtained for <u>baseline</u> runs of respective facility.
- Hg[2] is the average mercury oxidation obtained for 0.1wt% <u>ESORG-HG-11</u> runs or respective facility.

- Example using Minntac baseline and 0.1wt% average oxidations observed:
  - Hg[1] = Minntac baseline average oxidation = 24%
  - Hg[2] = Minntac 0.1wt% oxidation average = 62%

$$\% \text{ Hg Oxidation} = \frac{\{62-24\}*100}{\{100-24\}} = \underline{50\%}*$$

*Values might change slightly from values in report body and table below due to rounding.

2) Data Quality Assessment for Key Variables:

a) Not applicable. Mercury oxidation calculated based on results of each individual run.

b) Average values obtained for Hg[1] and Hg[2] are listed in Table 12 below.

c) Data will be stored at University of North Dakota – Institute for Energy Studies.

3) Mercury Removal Estimates:

a) Reduction potential for each plant is summarized in Table 13 below.

Table 12. Reduction Potential of ESORB-HG-11 for Each Taconite Facility.

Facility	Hg[1] (SD), %	Hg[2] (SD), %	Reduction Potential (SD), %
Minntac	24 (4.6)	62 (7.2)	49 (9.4)
Keetac	15 (2.5)	46 (3.8)	36 (4.5)
Arcelor Mittal	20 (1.0)	53 (10.2)	41 (12.7)
Utac	22 (3.5)	37 (5.5)	19 (7.1)
Hibtac*	15 (7.2)	52 (5.1)	43 (6.5)

Note: 1) The oxidation estimates, Hg[1] and Hg[2], are averages obtained during bench tests, and Hg[2] is assumed to estimate a “minimum” possible reduction expected for stack mercury emissions during full-scale scale work. 2) Only results for 0.1wt% ESORB-HG-11 loading are used to determine Hg[2] as this is considered the optimum loading. *Results for both standard and compression pellets averaged.

b) Qualitative Factors:

Gas phase oxidation was not quantifiable using bench scale test equipment, see report. Consequently, actual full-scale test reduction potential of the technology tested could be higher than that observed during bench tests.

c) Problems Encountered:

No significant problems were encountered during technology testing.