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A Pilot Study of Mercury Liberation and Capture from Coal-Fired Power Plant Fly Ash

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ABSTRACT

The coal-fired electric utility generation industry has been identified as the largest anthropogenic source of mercury (Hg) emissions in the United States. One of the promising techniques for Hg removal from flue gas is activated carbon injection (ACI). The aim of this project was to liberate Hg bound to fly ash and activated carbon after ACI and provide high-quality coal combustion products for use in construction materials. Both bench- and pilot-scale tests were conducted to liberate Hg using a thermal desorption process. The results indicated that up to 90% of the Hg could be liberated from the fly ash or fly-ash-and-activated-carbon mixture using a pilot-scale apparatus (air slide) at 538 °C with a very short retention time (less than 1 min). Scanning electron microscope (SEM) evaluation indicated no significant change in fly ash carbon particle morphology following the thermal treatment. Fly ash particles collected in the baghouse of the pilot-scale apparatus were smaller in size than those collected at the exit of the air slide. A similar trend was observed in carbon particles separated from the fly ash using froth flotation. The results of this study suggest a means for power plants to reduce the level of Hg in coal-combustion products and potentially recycle activated carbon while maintaining the resale value of fly ash. This technology is in the process of being patented.

IMPLICATIONS

ACI is a promising technology for capturing Hg from coal combustion flue gas. Concern has been raised regarding the increased Hg and carbon content in coal-combustion products as a result of ACI. This paper presents research results from a pilot study designed to liberate Hg from coal fly ash using a thermal desorption process. The Hg liberation process is intended to replace conventional air slide conveying units with a high-temperature version for material handling of fly ash or sorbents at power plants or other facilities.

INTRODUCTION

According to the U.S. Environmental Protection Agency's (EPA) 1997 Mercury Study Report to Congress, coal-fired electric utilities, municipal waste combustors, and medical waste incinerators are the highest emitters of mercury (Hg) to the air.[1] It is estimated that 75 tons of Hg are contained in the fuel burned annually at coal-fired power plants; currently, 60% is released to the atmosphere (atm) and the remaining 40% is removed by particulate and sulfur dioxide control devices.[2] On January 30, 2004, EPA proposed new rules to regulate Hg emissions from coal-fired power plants. Under EPA's proposal, power plants would be required to reduce Hg emissions from 48 tons to 15 tons nationwide by 2018.[3]

One of the most effective and widely accepted technologies for capturing Hg from flue gas emissions is to inject activated carbon into the gas stream. Injected activated carbon binds the vapor-phase Hg through physical adsorption and chemisorption and is collected in downstream particulate collection devices, such as fabric filters (FFs) and electrostatic precipitators (ESPs). Results from several tests indicate that the effectiveness of activated carbon injection (ACI) in removing Hg vapor depends on the type and composition of burned materials, flue gas composition and temperature, Hg speciation, activated carbon properties, injection rate, and operating conditions.[4] Powdered activated carbon can be injected into the flue gas upstream of the primary ESP or baghouse. However, the resulting activated-carbon-and-fly-ash mixture becomes unusable in concrete without beneficiation removing the activated carbon. The value of fly ash declines because of limited uses or the need for expensive beneficiation techniques such as froth floatation or electrostatic separation. Moreover, Hg captured by activated carbon may increase the potential to release Hg into the environment when reusing or landfilling fly ash.

At We Energies, ~650,000 tons of fly ash and bottom ash is produced every year and ~98% was beneficially reused in 2003. The primary uses of We Energies fly ash include cementitious material for concrete and concrete products, feedstock for Portland cement manufacturing, supplemental fuel, full depth reclamation of asphalt pavements, liquid waste stabilization, and soil stabilization.[5] Therefore, it is essential to maintain the high quality of fly ash for resale purposes. Another method of capturing Hg from flue gas emissions is to inject activated carbon into the flue gas downstream of the primary particulate collection device (ESP or baghouse) and ahead of a second particulate collection device. The activated carbon and Hg mixture is collected separately from the fly ash. Therefore, the quality of fly ash is preserved for use in concrete. This approach also has the potential to separate Hg captured on activated carbon and allow activated carbon to be regenerated and reused.

In this research, a pilot scale apparatus was designed and used to liberate mercury from fly ash and activated carbon by thermal desorption. The separation of mercury from fly ash and activated carbon is important for two reasons. First, it allows potential mercury sorbent regeneration and reuse. The cost of carbon injection is very high, ranging from $5000 to $70,000 per pound of Hg removed according to the Mercury Study Report to Congress.[1] This cost can be reduced significantly whether activated carbon is regenerated and reused. Second, it maintains the high quality of fly ash for reuse in concrete and cement manufacturing. The stability of Hg on fly ash samples from three power plants (Presque Isle Power Plant, Valley Power Plant, and Pleasant Prairie Power Plant) was examined in this study. The ash from Pleasant Prairie was obtained after a test sponsored by the Department of Energy National Environmental Technology Laboratory and the Electric Power Research Institute. It contained activated carbon for enhanced Hg control. Bench and pilot experiments were done to determine the optimum operating conditions for Hg liberation. In addition, a scanning electron microscope (SEM) was used to examine the impact of thermal treatment on the morphology of carbon and fly ash particles.

EXPERIMENTAL METHODS

Dry ash samples from three different power plants were collected and stored in clean glass bottles for laboratory study. Fly ash samples from Presque Isle Power Plant (PIPP) and Valley Power Plant (VAPP) were derived from a western bituminous coal and collected in precipitators and baghouses, respectively. Fly ash samples from Pleasant Prairie Power Plant (PPPP) were derived from subbituminous coal and collected using ESP. The source and characteristics of each ash sample are shown in Table 1.

Bench-Scale Feasibility Study

A bench-scale study was done to select an optimum combination of temperature and retention time to maximize Hg recovery. Fly ash samples taken from PIPP were used in the experiments. The total Hg concentration in the sample was determined by cold-vapor generation atomic fluorescence spectroscopy (AFS). Samples were treated in a muffle furnace in an inert atmosphere at different temperatures ranging from 371 °C to 538 °C for retention times of 1–5 min. A nitrogen atmosphere was maintained to keep the carbon from igniting. The percent of Hg liberated from the ash samples was determined by measuring the total Hg left in the ash after thermal treatment.

Pilot-Scale Study

Based upon the test results obtained from the bench-scale study, a test program was designed to generate experimental data from a pilot apparatus (Figure 1).

The pilot test apparatus is composed of seven main components: cone-shaped hopper, air slide, baghouse, burner, collector underneath the air slide, Hg condenser, and wet scrubber. During each fly ash processing run, samples were fed into the air slide through the cone-shaped hopper. The speed of sample going through the system was controlled by a rotary feeder. Inside the air slide, samples were heated by hot air coming from the burner. The temperature inside the air slide was controlled by adjusting the airflow rate of the burner. A data logger connected to five thermocouples located at the burner, baghouse inlet, and the inlet, midpoint and outlet of the air slide, was used to record the temperature readings. After traveling through the air slide, part of the sample went to the collector at the discharge end of the

Table 1. Fly ash sample sources and characteristics.

Ash Sample	Coal/Ash Description	Total Hg (ppm)	LOI (%)	Chlorine (ppm)	Sulfur (%)
PIPP-I	Bituminous fly ash from ESP	0.180	26.7	133.5	0.68
PIPP-II	Bituminous fly ash from ESP	0.150	21.7	17.9	0.43
PPPP	Subbituminous fly ash + activated carbon from ESP	0.970	3.2	225.5	1.24
VAPP	Bituminous fly ash from baghouses	0.200	33.5	133.5	0.68

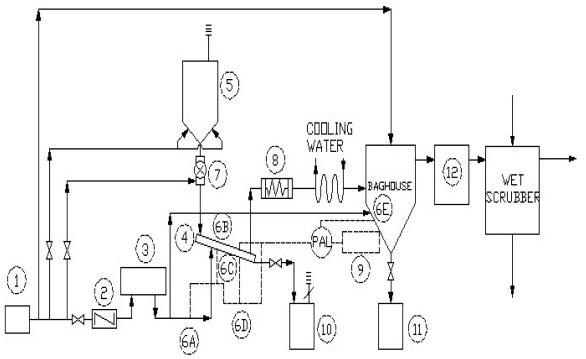

Figure 1. Pilot-scale apparatus for Hg liberation and capture. (1) Air supply; (2) heat exchanger; (3) 1500 °C furnace; (4) air slide; (5) fly ash feeder; (6) thermal couples; (7) rotary feeder; (8) heat exchanger; (9) control panel; (10) ash collect drum; (11) ash collect drum; (12) Hg condenser.

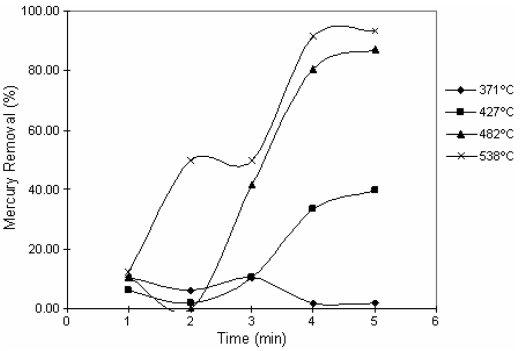

Figure 2. Bench-scale study on the effect of temperature and retention time on Hg removal from PIPP fly ash.

air slide and the rest of the sample went to the baghouse. Samples in this pilot unit study that were collected under the discharge end of the air slide represent the "product" and the samples collected under the baghouse represent a "byproduct" that can possibly be reintroduced for retreatment in the process or be disposed. Hot air that exited the baghouse passed through a mercury condenser and a wet scrubber before being emitted into the ambient environment. Fly ash samples from PIPP, VAPP, and PPPP were used for the pilot study. Hg concentration and carbon content were measured before and after thermal treatment for comparative purposes. Loss on ignition was used as an estimate of carbon content.

SEM Analysis

One of the objectives of this project was to determine whether the thermal treatment had any impact on the morphology of carbon and fly ash particles, because particle morphology can influence Hg adsorption. A SEM coupled with energy dispersive X-ray microanalysis was used to obtain representative images of ash samples before and after the pilot treatment. Because many studies indicated that carbon in ash is primarily responsible for Hg sorption,[5–10] we separated the carbon from one of the ash samples and further examined the effects of thermal treatment specifically on carbon particles. The VAPP treated fly ash sample was sent to the Institute of Materials Processing at Michigan Technological University and separated into inorganic and carbon fractions by froth flotation.

RESULTS AND DISCUSSION

Bench-Scale Feasibility Study

Figure 2 shows the rate of Hg removal from PIPP fly ash in the muffle furnace using different combinations of temperature and retention time. PIPP fly ash Units 5 & 6 was derived from western bituminous coal and collected using a precipitator. The original total Hg concentration in the sample was 0.42 ppm. The results indicated that both temperature and retention time are important parameters in the thermal desorption process. At temperatures lower than 482 °C, the max Hg removal was 40% even with prolonged thermal treatment. More Hg can be removed with higher temperature and longer treatment. The relationship between mercury removal rate and retention time appeared to be S shaped when temperatures higher than 371 °C were used. At 538 °C, 90% of the Hg was liberated from the fly ash within 4 min.

Pilot-Scale Study

A total of 10 fly ash samples from three different power plants were used in the pilot study. The pilot study was conducted in two phases: first, ash samples (two from PIPP, one from PPPP, and one from VAPP) were treated in the pilot scale apparatus under fixed temperature and rotary feeding rate (retention time); second, fly ashes (three split samples from PIPP and three split samples from PPPP) were tested under different temperatures and rotary feeding speed. The Hg concentrations in these fly ash samples ranged from 0.11 ppm to 1 ppm. Samples from PPPP were a mixture of activated carbon and fly ash obtained during the previous EPRI/DOE ACI demonstration study. For each test in phase one, the initial temperature of the air slide inlet was set at 538 °C and the rotary feeding speed was set at 1000 rpm. The results of these tests are shown in Table 2 and Figure 3. All four initial tests indicated that Hg could be liberated from various ash samples at 538 °C using the pilot scale apparatus. The majority of the sample passing through the air slide discharged to the collector under the air slide with very low concentrations of Hg detected in these samples. A small proportion of the sample passed with the airflow to the baghouse and contained a relatively high Hg content.

The Hg concentrations in fly ash collected under the air slide were 74.4–85.6% lower than those found in the original ash samples. In contrast, Hg concentrations in ash collected in the baghouse showed 90–113.3% increases compared with the original samples except for the

Table 2. Hg liberation from PIPP, PPPP, and VAPP samples with air slide inlet temperature 538 °C, and rotary feeding speed 1000 rpm (pilot test Phase I).

Sample Description	PIPP-I	PPPP	VAPP	PIPP-II
Samples collected before experiment				
Hg content (ppm)	0.180	0.970	0.200	0.150
LOI (%)	26.7	3.2	33.5	21.7
Sample weight (lb)			16.5	
Samples collected under the air slide				
Hg content (ppm)	0.046	0.140	0.031	0.031
Hg removed (%)	74.44	85.57	84.50	79.33
LOI (%)	38.1	9.8	36.9	26.1
Sample weight (lb)			14.5	
Samples collected under the baghouse				
Hg content (ppm)	0.380	1.000	0.380	0.320
Hg increased (%)	111.11	3.09	90.00	113.33
LOI (%)	22.6	10.5	26.9	22.0
Sample weight (lb)			4.3	

PPPP sample that only had a 3% increase. It is possible that particles with higher Hg content went up to the baghouse along with the airflow and particles with lower Hg concentration went down the air slide. However, data from loss on ignition (LOI) analysis indicated that samples collected under the air slide had higher amounts of carbon than did samples collected by the baghouse. Because many studies suggested that carbon in fly ash is primarily responsible for Hg sorption, it is unlikely Hg went to the baghouse merely because of the physical separation of fly ash particles.

To determine the amount of Hg desorbed, the mass of each sample was recorded to calculate the mass balance of Hg and carbon in the VAPP experiment. The recorded mass of samples before and after experiment and detailed mass balance analysis are shown in Table 2. The mass balance can be used as an estimation of how Hg and carbon partitioned during the process. It is assumed that Hg desorbed was collected by the condenser, because ambient air analysis indicated no detectable Hg.

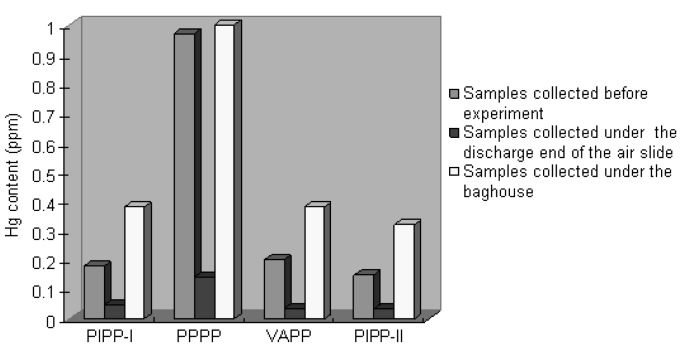

Figure 3. Pilot-scale study of Hg liberation from PIPP, PPPP, VAPP samples with an air slide inlet temperature of 538 °C and a rotary feeder speed of 1000 rpm.

For the PPPP sample, the Hg concentration in samples collected in the baghouse was similar to the Hg concentration found in the original samples (1 ppm). This may be explained by the activated carbon present in the PPPP sample that could re-adsorb the liberated Hg. Nonetheless, the amount of Hg that was collected in the baghouse only represents a small proportion of the total Hg in the untreated sample because the majority of the sample mass went to the collector under the air slide.

Another possible scenario was that liberated Hg might become re-adsorbed onto the fly ash inside the baghouse. Studies have shown that Hg capture on the fly ash proved to be a function of the amount of carbon in the fly ash within each collection system and of the collection temperature within the individual collection systems, the cooler baghouse collection system having more Hg in the fly ash despite lower carbon content.[9] The temperature in the baghouse might have played a role in condensing Hg back onto fly ash.

Further experiments were performed to determine how temperature and rotary feeding speed would impact the Hg desorption process using PIPP and PPPP samples. Three experiments were run with the rotary feeder speed set at 800, 1000, and 1200 rpm and the air slide inlet temperature set at 538 °C using PIPP samples. The initial Hg content in these samples was around 0.14 ppm. PPPP samples were treated with different heating temperatures, 538 °C, 593 °C, and 649 °C and the rotary feeder speed fixed at 1000 rpm and. The results are shown in Table 3.

A comparison of Hg content in PIPP samples treated with different rotary feeder speed and constant temperature is shown in Figure 4. Data analysis shows no obvious

Table 3. Effects of temperature and rotary feeding speed on Hg liberation from PIPP and PPPP samples (pilot test Phase II).

Sample Description	PIPP			PPPP		
Rotary Feeder Speed (rpm)	800	1000	1200	1000	1000	1000
Temperature (°C)	538	538	538	538	593	649
Samples collected before experiment						
Hg content (ppm)	0.140	0.140	0.110	0.690	0.620	1.000
LOI (%)	25.7	25.3	26.6	2.7	2.6	2.7
Samples collected under the air slide						
Hg content (ppm)	0.025	0.015	0.025	0.100	0.054	0.055
Hg removal (%)	82.14	89.29	77.27	85.51	91.29	94.50
LOI (%)	42.3	31.3	14.6	3.2	1.9	1.8
Samples collected in the baghouse						
Hg content (ppm)	0.380	0.400	0.360	0.810	1.200	1.400
Hg increased (%)	171.43	185.71	227.27	17.39	93.55	40.00
LOI (%)	22.7	20.9	20.5	5.3	3.9	4.0

correlation between the rotary feeding speed and Hg removal. The Hg content in fly ash samples collected under the air slide was 77–89.3% lower than that found in the original samples. It is possible that rotary feeder speed does not significantly impact the retention time of samples in the air slide.

The retention time of fly ash in the air slide is also dependent on the airflow rate and the design of the air slide. We noticed that the actual retention time of fly ash in the air slide was less than 1 min, which was considerably shorter than the optimum retention time suggested by the bench-scale tests. The difference could be explained by the fact that ash samples in the air slide had much more surface area exposed to the hot air than ash samples in the muffle furnace. Another possible reason is that the retention time was already long enough for the desorption process to be completed, so extended treatment could not have liberated more Hg from the ash samples.

Analysis with PPPP samples indicated that more Hg was liberated when the treatment temperature was higher. As shown in Figure 5, the highest Hg removal rate was achieved when the air slide inlet temperature was set at 649 °C. Figure 6 shows the recorded temperature of the burner, air slide inlet, air slide midway, air slide outlet, and baghouse. There was a temperature drop at the air slide inlet when ash was added. This may explain why the optimum temperature observed in the pilot tests was higher than the optimum temperature found in bench-scale study. Hg in the samples collected from the baghouse increased significantly, especially for PIPP samples, which is consistent with the test results obtained from earlier experiments. In addition, to increase the temperature of the trials, a change was made to the airflow that may have inadvertently increased the retention time, again increasing the amount of mercury removed from the ash. The total

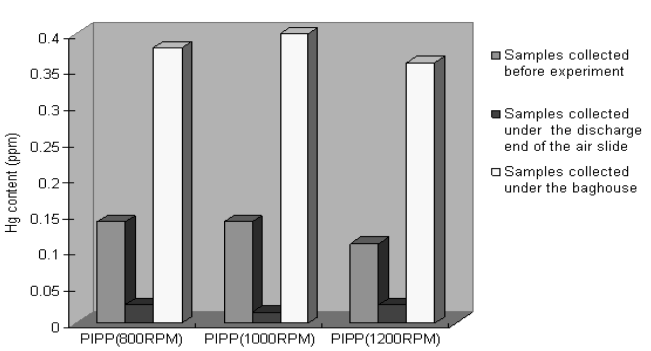

Figure 4. Pilot-scale study of Hg liberation from PIPP samples with an air slide inlet temperature of 538 °C and rotary feeder speeds of 800, 1000, and 1200 rpm.

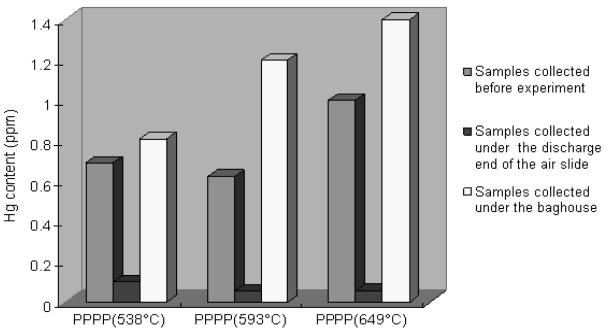

Figure 5. Pilot-scale study of Hg liberation from PPPP samples with a rotary feeder speed of 1000 rpm and air slide inlet temperatures of 538, 593, and 649 °C.

amount of Hg re-adsorbed onto particles in the baghouse was not significant. However, it should be considered in future design of the apparatus and experiments.

SEM Analysis of Samples Obtained in Pilot Study

An SEM coupled with energy dispersive X-ray microanalysis was used to obtain representative images of ash samples before and after the thermal treatment. Figure 7 shows the image of original VAPP sample. The white particles in the pictures are mainly inorganic fly ash compounds (Si and Al). The darker particles are mostly composed of carbon. The black background represents the spaces between the particles. The carbon particles are easily visible because VAPP fly ash has relatively high carbon content (LOI −33.5%). Images of VAPP sample collected after the air slide and in the baghouse following treatment are shown in Figures 8 and 9. It is apparent that the overall particle size is larger in fly ashes collected from the air slide than those collected in the baghouse. Figures 10 through Figure 12 show the SEM images of VAPP samples that contain higher carbon contents after froth flotation. The carbon particles collected from the air slide are much bigger than those collected in the baghouse. The carbon particles from the air slide, with sizes ranging

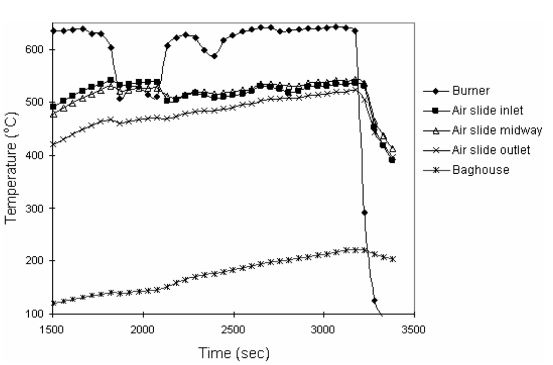

Figure 6. Recorded temperature curve for test on PPPP sample, with an air slide inlet temperature of 649 °C and a rotary feeder speed of 1000 rpm.

from 40 μm to as large as 200 μm, are quite different from those floc-like, fine carbons collected in the baghouse. It is likely that the significant change in carbon particle morphology was a result of chemical treatment used in the froth flotation process.

CONCLUSIONS

The following conclusions can be drawn from the results of bench- and pilot-scale studies:

- The pilot-scale apparatus is effective in removing Hg from fly ash samples with thermal treatment. In the early trials, the majority of the sample introduced passed through the air slide with very low concentrations of Hg detected in these samples.
- Both bench- and pilot-scale experiments indicated that Hg removal is favored by higher temperatures.
- In bench-scale studies, longer retention time seemed to favor the thermal desorption process. Data analysis with pilot experiments shows no direct link between rotary feeding speed and Hg removal. It is possible that rotary feeder speed does not correlate directly with retention time.

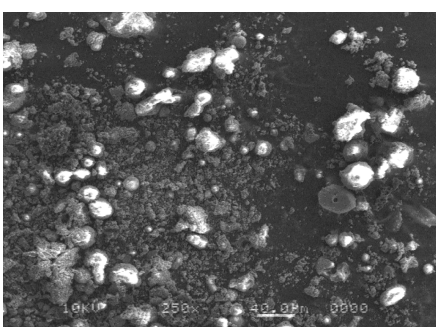

Figure 7. SEM image of VAPP before the thermal treatment (250×).

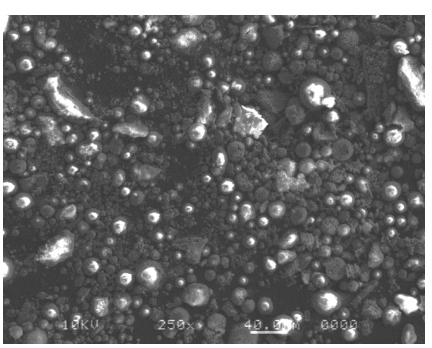

Figure 8. SEM image of VAPP collected under the baghouse after the thermal treatment (250×), air slide inlet temperature 538 °C, and rotary feeder speed 1,000 rpm.

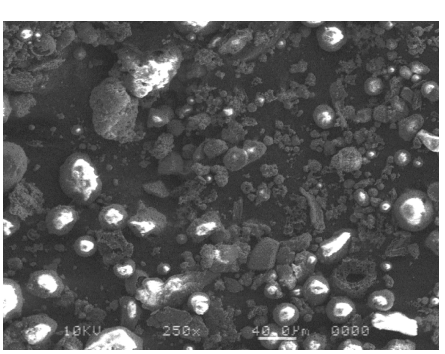

Figure 9. SEM image of VAPP collected under the air slide after the thermal treatment (250×), air slide inlet temperature 538 °C, and rotary feeder speed 1,000 rpm.

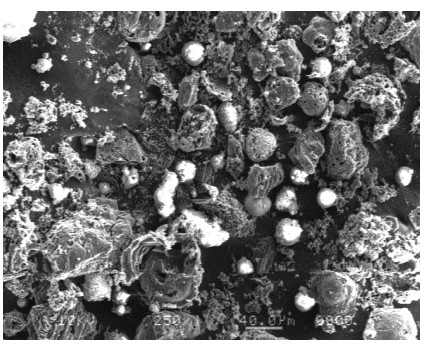

Figure 10. SEM image of VAPP before the treatment (high C part, 250×).

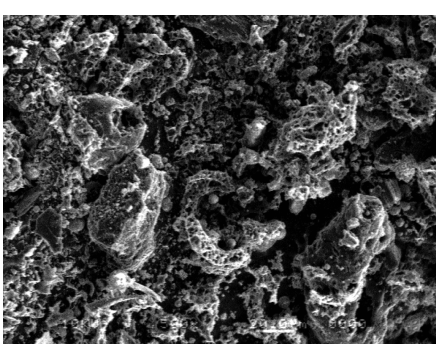

Figure 11. SEM image of VAPP collected under the baghouse after the thermal treatment (high C part, 250×), air slide inlet temperature 538 °C, and rotary feeder speed 1,000 rpm.

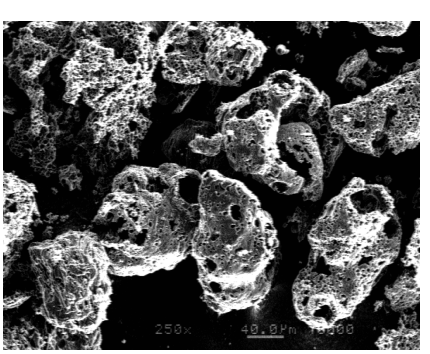

Figure 12. SEM image of VAPP collected under the air slide after the thermal treatment (high C part, 250×), air slide inlet temperature 538 °C, and rotary feeder speed 1,000 rpm.

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