Technique for Determining the Potential Recovery of Carbon from Flyash

Paul H. Zandhuis[1], Michael V. Ciocco[1], Richard P. Killmeyer[2], McMahan L. Gray[2], Yee Soong[2]

[1]Parsons Project Services Inc., National Energy Technology Laboratory, P.O. Box 618, South Park, PA 15129; [2]US Department of Energy, National Energy Technology Laboratory, P.O. Box 10940, Pittsburgh, PA 15236

Email & Phone: paul.zandhuis@netl.doe.gov 412-386-4712, michael.ciocco@netl.doe.gov 412-386-4711, richard.killmeyer@netl.doe.gov 412-386-6409, mcmahon.gray@netl.doe.gov 412-386-4826, yee.soong@netl.doe.gov 412-386-4925

Fax Number: 412-386-4810

Abstract

In the search for utilization of unburned carbon from flyash, flotation has been considered by many as a possible method for reclaiming the carbon. Due to the ever-increasing need to minimize landfill materials and reutilize waste streams, NETL has reviewed flyash flotation techniques in an effort to develop a methodology for determining the floatability potential of the carbonaceous material. This methodology was employed on a flyash generated from the Reliant Energy Shawville power plant. A variety of variables were adjusted in order to delineate their effects on the flotation potential of this flyash. The variables included pH, ultrasonic treatments, collector conditioning, promoters and dispersants. The techniques utilized clearly show which variables were the most important in optimizing the flotation potential for this flyash.

Introduction

The NETL (National Energy Technology Laboratory) has focused efforts on obtaining a high quality carbon from a waste product of coal-fired electric power generation. The recovered carbon can be used as a sorbent in some applications that use activated carbon, and at the same time, the reduction of carbon from the flyash increases the pozzolanic quality of the gangue and generates another high quality feed material for the production of Portland cement. Robl et al. showed that the production of a high quality pozzolan could be generated from a ponded flyash [1]. In fact, several patents have been filed to document flotation process variables that enhance the yield and quality of the carbon and the pozzolan. Aunsholt K.E.H. [2] has a U.S. Patent which reduces the pH of flyash slurry prior to flotation to increase the carbon recovery. Minkara & Heavilon showed that ultrasonic conditioning of the flyash slurry prior to flotation enhances the flyash as a pozzolan for Portland cement mixes [3]. These two factors (pH & ultrasound) were just some of the variables that were tested with this Shawville flyash flotation.

The ability to reclaim carbon material using techniques such as flotation has now been widely demonstrated. However, there is no standard laboratory technique for determining the floatability potential of coal, or of carbon from flyash. For this reason, NETL recently conducted a study to compare different coal flotation techniques. [4] In the study, several different labs conducted their own flotation methods on identical samples. The results showed that there was great disparity between the labs and that the particular laboratory technique is critical to optimizing the grade/recovery curve for flotation. Based on this result, NETL extended the study to examine which factors may help or hinder the grade/recovery curve for flyash. This paper reports on the results of variables which affect the Shawville flyash floatability potential.

Experimental

Sample; NETL obtained four drums of flyash from the combustion of a bituminous coal at the Reliant Energy plant located in Shawville, PA. NETL conducted a long piling, coning, and quartering method to split drums of the Shawville flyash down representative 150 gram increments. The feed sample was typically 40% moisture and 83% ash (dry basis). The nominal size of the flyash was 48x0 mesh (US) with 30% of the material below 500 mesh (US).

Equipment; The apparatus used in flotation was a Denver 4 liter laboratory flotation cell. The ash analysis was performed with a LECO TGA-601 (Thermo-Gravimetic-Analyzer). The sonication device was a Branson Sonifier 450, model 132137. The Sonifier operated at a nominal frequency of 20 kHz.

Flotation procedure; The procedure is similar to release analysis, however it is conducted in reverse. The sample is first floated in the cell to exhaustion (meaning no more material floats), followed by the concentrate being refloated to exhaustion two more times with the three tailings combined. The concentrate that remains is again placed in the Denver cell and floated at a fairly severe (high aeration and impeller rate) condition. The remaining tailings are saved separately and the concentrate again placed in the Denver cell. This flotation and saving of tailings is repeated with each subsequent test being at lower severity (i.e. lower aeration and/or impeller rates) until no further float material is reporting over the weirs. This procedure was chosen because it showed one of the best grade/recovery curves in the previously mentioned NETL study [4].

Results and Discussion

The testing encompassed varying the dosages of flotation agents, ultrasonic conditioning treatments and pH adjustments. Typically, the “reverse” release analysis is conducted with an excess of frother to ensure that the maximum flotation is achieved. However, the amount of collector is critical to the optimum flyash flotation. This testing was conducted with polyproplyene glycol as the frother (in excess, 100-150 ppm) and kerosene as the collector. The kerosene was added to the slurry prior to any flotation steps. The collector conditioning was conducted in each of the flotation tests for 10 minutes unless otherwise noted. In most of the literature, petroleum sulfonate was used as a promoter for enhancing the flyash flotation. Due to a lack of commercial distributors of this product, it was omitted from this study.

Collector: Initially, flotation tests with varying collector dosages (from 0.32 to 20lbs/ton) were conducted to optimize the grade/recovery curve. The results of the collector dosage study indicated that 10lbs/ton was a sufficient dosage to achieve the maximum grade/recovery curve. Additionally, the collector conditioning time was varied to determine optimal conditioning with kerosene. It was found that 30 minutes of conditioning was the optimal time. However, to keep all of the variables consistent with some of the earlier testing, the conditioning time of 10 minutes was held constant throughout the remainder of the tests.

pH testing: Once the collector dosage for maximum recovery and quality was achieved, the effect of pH was observed. The pH of the slurry (naturally about 7.5) was adjusted after the conditioning step with the kerosene and prior to the first flotation. The pH was adjusted with either concentrated ammonium hydroxide or concentrated hydrochloric acid. The pH adjustment was done once prior to the flotation and then the slurry was allowed to drift to a neutral pH with the ensuing dilutions. A minimum pH of 2 was chosen due to the large volume of concentrated HCl required for the testing. The low pH could prove to be hazardous to the operator and be economically unfeasible. The results from the pH study compare well with the literature, Minkara [3]. That is, as the pH of the flyash slurry dropped below 7 the separation continued to improve. Accordingly, as the pH was raised above 7 the separation deteriorated.

Ultrasonic testing: In this series of flotation tests, flyash/water slurries were treated with ultrasound. The kerosene was added to the slurry and then it was subjected to ultrasonic treatment. No other conditioning was conducted upon the flyash. The length of ultrasonic treatment was varied to illustrate the effectiveness of this parameter. In order to evaluate the concern of the degree of sample attrition with increasing ultrasonic treatment, NETL conducted wet screening of sonicated samples. Ultrasonic treatment for 1 minute showed an improvement in the separation with no size reduction. However, longer treatment times (5 minutes and longer) showed significant improvements in the grade/recovery curve which was presumably due to the liberation of unburned carbon as a result of size reduction. The wet screen analysis of the sonicated samples showed no selectivity of ash liberation within the size fractions. In addition, several flyash samples were placed in a jar mill to compare the two size reduction methods. The size analysis showed similar carbon liberation between the jar mill and the ultrasonic treatments.

Dispersant testing: NETL also observed the effects of adding a dispersant into the flyash slurry. Dispersant dosages were varied to study the optimal effect of dispersants in the flotation. Aerofloat Sodium Promoter, OT-75 (a diothiophosphate salt) was used as the dispersant. The dispersant and collector were added at the same time and allowed to condition for 10 minutes. The effect of the dispersant to the grade/recovery curve was marginal. However, it should be noted that excessive loading of the dispersant (above 500 ppm) reduced the quality of the separation.

4. Conclusions

This study showed that the particular steps in a laboratory flotation technique, and the levels of key operating, reagent, and surface chemical variables, could significantly impact the resulting grade/recovery curve. This can present a misleading picture of the potential recovery and purity of the carbon and ash products that might be produced. The particular findings from this study were that:

A. The optimal collector dosage was 10#/ton and the optimal conditioning time was 30 minutes.

B. Reduction of pH below 7 enhanced the grade/recovery curve.

C. Ultrasonic conditioning improved the grade/recovery curve from a conditioning standpoint, however, excessive treatment can result in size reduction that liberates the embedded carbon from the flyash.

D. The addition of dispersants gave a marginal improvement to the grade/recovery curve.

References

[1] Robl, T.L., J. Groppo, U. Graham, C.J. McCormick, T.F. Edens, S.S. Medina, "The Production of High Quality Pozzolan from Ponded Flyash," Proceedings of Conference on Unburned Carbon on Utility Flyash, Pittsburgh, PA, May 1997

[2] Aunsholt, K.E.H., U.S. Patent 4,426,282, January 17, 1984

[3] Minkara, R.Y., J.L. Heavilon, U.S. Patent 5,988,396, November 23, 1999

[4] Killmeyer, R.P., M.V. Ciocco, and P.H. Zandhuis, "Comparison of Procedures for Determining the Floatability Potential of Fine Coal," Proceedings of Coal Prep '00, Lexington, KY, May 2000.

[5] Gray, M.L., K.J. Champagne, Y. Soong, R.P. Killmeyer, M. Maroto-Valer, J.M. Andresen, M.V. Ciocco, and P.H. Zandhuis, "Single-Stage Cleaning of Flyash," Proceedings of the Pittsburgh Coal Conference, Pittsburgh PA, September 2000.