# Asian Ash Characteristics and Use for Portland/Calcium Sulfoaluminate Hybrid Cements

**Tristana Y. Duvallet [1], Robert B. Jewell [1], Anne E. Oberlink [1], Thomas L. Robl [1], David Harris [2]**

[1] University of Kentucky, Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY, 40511, USA
[2] Asian Coal Ash Association, Australia/China, Beijing, China

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## ABSTRACT

This paper summarizes the use of two different ashes in the synthesis of Portland/Calcium Sulfoaluminate (OPC/CSA or A/CSA) cements. These ashes are a Shentou ponded coal ash from the Shanxi Province in China and a “fresh” Mongolia fly ash. Their chemical compositions highly differ, especially the $SiO_2$ and $Al_2O_3$ contents, being respectively 47.26 wt.% and 37.10 wt.% for the Shentou ponded coal ash, and 29.17 w.% and 48.41 wt.% for the Mongolia fly ash. The high contents of both silica and alumina make both ashes perfect candidates for the production of OPC/CSA clinkers. These particular hybrid clinkers are composed mainly of alite ($C_3S$) and calcium sulfoaluminate ($C_4A_3\acute{S}$), both phases responsible for the high early strength development in OPC and CSA cements, respectively. The production of high quality OPC/CSA clinkers were produced with both ashes with the addition of hydrated lime, FGD gypsum, fluorite, and bauxite, at 1250°C for 60 minutes: 40.2 wt.% $C_3S$, 21.3 wt.% $C_2S$, 3.2 wt.% $C_4AF$, and 32.0 wt.% $C_4A_3\acute{S}$ with the Shentou ponded coal ash; and 29.3 wt.% $C_3S$, 21.4 wt.% $C_2S$, 2.0 wt.% $C_4AF$, and 43.3 wt.% $C_4A_3\acute{S}$ with the Mongolia fly ash.

## 1. INTRODUCTION

As per the International Energy Agency (IEA) report from 2016 [1], China is the world’s leading coal producer, with 3527.2 Mt of coal produced in 2015, representing nearly half of the world’s production of coal at 7708.7 Mt, as shown in Figure 1. Consequently, the necessity to reuse and/or recycle coal combustion by-products, such as fly ashes, instead of landfilling this material, is of high priority for the country.

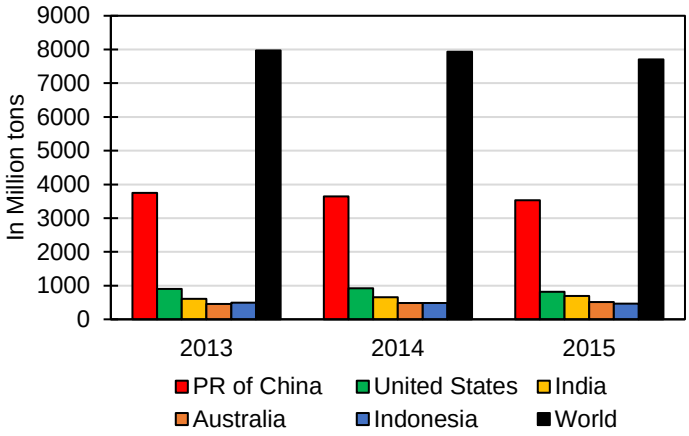


*Figure 1. Major coal producers* [1]

In this paper, two sources of coal ash are characterized: 1) a ponded coal ash from the 4 x 500-MW Shentou Second Power Plant, located in Shuozhou City in the Shanxi Province in China; and 2) a "fresh" (meaning not landfilled or ponded) coal ash from the Zhungeer Power Plant, located in the Ordos City, at the junction of Shanxi, Shaanxi, and Mongolia Provinces, in Inner Mongolia in China. [2] Following the characterization of both ashes, their potential use as raw material for the production of Portland/calcium sulfoaluminate (OPC/CSA or A/CSA) cements is assessed.

## 2. CHARACTERISTICS OF ASIAN ASH POND

### 2.1. Chemical Properties

The chemical composition of both ashes was determined by X-ray Fluorescence (XRF) following ASTM C4326-13 [3], and the results are presented in Tables 1 and 2. Both ponded and fly ashes are very similar in terms of oxide contents, with the exception of $SiO_2$ and $Al_2O_3$. The ponded ash contains more $SiO_2$ than the fresh ash, and the fresh ash contains more $Al_2O_3$ than the ponded ash. Both ashes are class F fly ash [4], due to their total content of ($SiO_2$+$Al_2O_3$+$Fe_2O_3$) being above 70 wt.%.

*Table 1: Major oxide composition of the Shentou ponded coal ash and the Mongolia fly ash, in weight percentage*

| In wt.% | CaO | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $SO_3$ | MgO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **Shentou** | 3.94 | 47.18 | 39.11 | 4.33 | 1.61 | 0.62 | 0.05 | 0.49 | 0.14 | 1.18 |
| **Mongolia** | 4.00 | 32.82 | 54.46 | 2.76 | 1.41 | 0.59 | 0.05 | 0.42 | 0.22 | 1.94 |

*Table 2: Trace elements in the composition of the Shentou ponded coal ash and the Mongolia fly ash, in weight part per million*

| In ppm | As | Ba | Cd | Co | Cr | Cu | Mo | Mn | Ni | Pb | Rb | Sb | Sr | V | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Shentou** | <1 | 240 | <1 | 12 | 56 | 15 | 184 | 174 | 13 | 40 | 270 | 4 | 458 | 154 | 32 | 317 |
| **Mongolia** | 8 | 278 | <1 | 19 | 54 | 31 | 221 | 160 | 1 | 76 | 468 | 5 | 1213 | 359 | 58 | 597 |

Based on X-ray diffraction (XRD) analyses, both ashes contain amorphous materials, as well as mullite, ettringite, gypsum, calcite, and quartz. The particularity is the presence of calcium aluminate ($CA_2$) and alumina ($Al_2O_3$) in the fly ash from Mongolia.

### 2.2. Physical Properties

The particle size distribution of both ashes is presented in Figure 2. The Shentou ponded coal ash was not easily separated and most of the ash particles (82 wt.%) were between 75 and 300 microns (µm), which may be due to the agglomeration of particles via solution and precipitation of gypsum in the pond. The Mongolia fly ash, on the opposite, was easy to sieve, and most of the particles, 85 wt.%, were below 75 microns (µm).

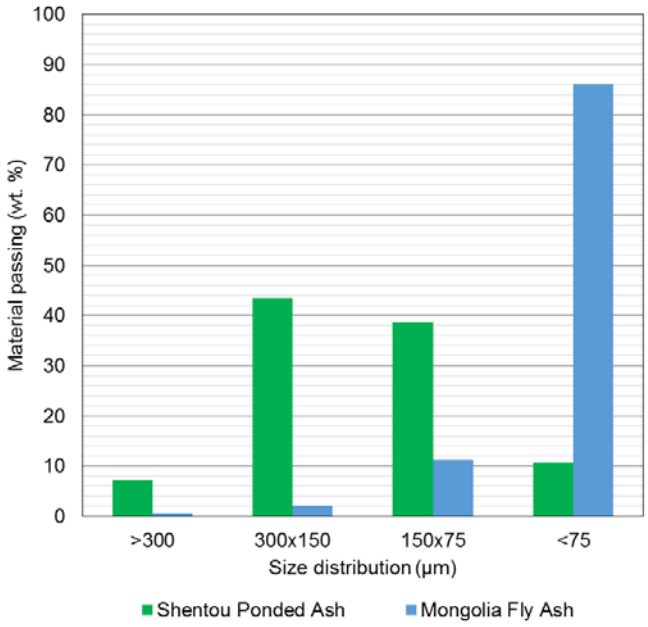


*Figure 2. Particle size distribution of Shentou ponded ash and Mongolia fly ash.*

The shape of the particles from both ashes was analyzed with an optical microscope and a scanning electron microscope (SEM). Particles from the Shentou ponded ash were both angular and spherical, as shown in Figures 3 and 5. The particles of Mongolia fly ash were mostly angular, with no spherical particles present, as seen in Figures 4 and 6.

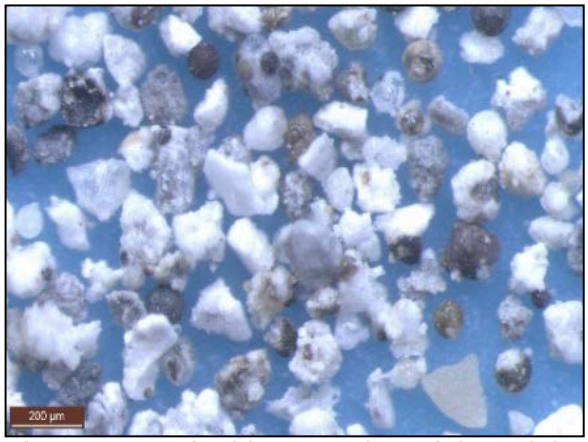


*Figure 3. Optical image of particles of the Shentou ponded ash*

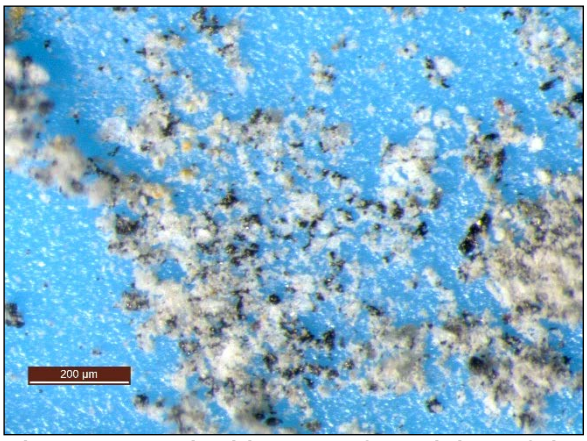


*Figure 4. Optical image of particles of the Mongolia fly ash*

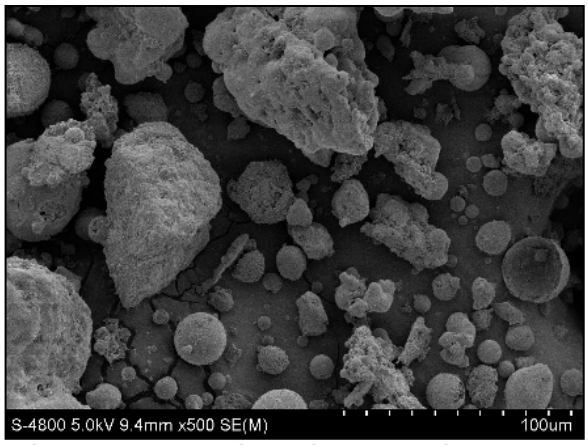


*Figure 5. Scanning Electron Microscope (SEM) image of particles of the Shentou ponded ash*

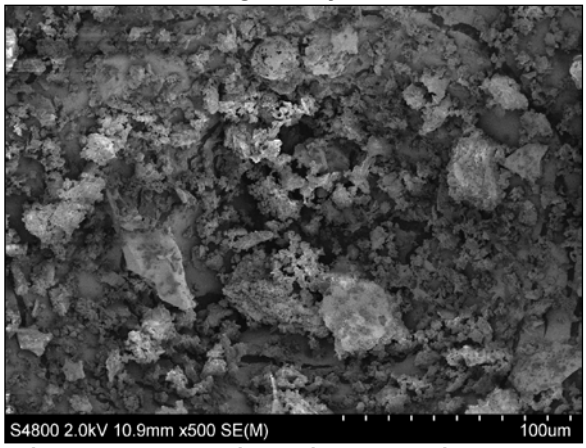


*Figure 6. Scanning Electron Microscope (SEM) image of particles of the Mongolia fly ash*

Both Shentou ponded ash and Mongolia fly ash are excellent candidate for use as raw materials for the production of Portland/calcium sulfoaluminate clinkers, as per their chemical composition with high content of both aluminum oxide and silicon dioxide.

## 3. USE OF PONDED AND FLY ASHES FOR THE PRODUCTION OF PORTLAND/CALCIUM SULFOALUMINATE HYBRID CEMENTS

OPC/CSA hybrid cements are composed mainly of alite ($C_3S$) and calcium sulfoaluminate ($C_4A_3\acute{S}$, ye'elimite, or also called Klein's compound), which are both the major clinker phases in Portland and calcium sulfoaluminate cements, respectively. Both $C_3S$ and $C_4A_3\acute{S}$ are responsible for the strength development in their respective cement composition: $C_3S$ hydrates to calcium silicate hydrate C-S-H responsible for most of the strength in Ordinary Portland cement (OPC); and $C_4A_3\acute{S}$ hydrates to ettringite which is responsible for the high early strength development in CSA cements.

### 3.1. Composition and Procedures

The materials, as well as their quantities used for the production of OPC/CSA clinkers are shown in Table 3. Their final theoretical clinker compositions are also detailed in Table 3. For the production of OPC/CSA clinker: from the Shentou ponded ash, hydrated lime, FGD gypsum, and bauxite were used as raw materials; from the Mongolia fly ash, hydrated lime and FGD gypsum were used. Fluorite was added to improve the formation of alite ($C_3S$) and assure that $C_3S$ coexists with calcium sulfoaluminate ($C_4A_3\bar{S}$). [5] The raw materials were mixed in a mortar and pestle until complete homogenization, with addition of deionized water (10 wt.%). Small 28x7 mm disks were then produced with a load of approximately 25000 lbs, and dried in an oven at 60°C for a few hours. The disks were placed in a platinum crucibles and fired at 800°C for 30 minutes, followed by 1200/1250°C for 60 minutes, and finally quenched in air. Samples were crushed in a shatter box and submitted for X-ray diffraction/Rietveld analyses to quantify the clinker composition.

*Table 3. Compositions of OPC/CSA clinkers made with Shentou ponded ash and Mongolia fly ash with their respective theoretical final clinker compositions.*

| **Raw Materials (wt.%)** | **With Shentou Ponded Ash** | **With Mongolia Fly Ash** |
|---|---|---|
| **Hydrated Lime** | 65.5 | 58.4 |
| **FGD Gypsum** | 6.3 | 9.7 |
| **Bauxite** | 5.0 | - |
| **Shentou Ponded Ash** | 22.5 | - |
| **Mongolia Fly Ash** | - | 31.3 |
| **Fluorite** | 0.7 | 0.6 |
| | | |
| **Theoretical Clinker Composition (in wt.%)** | | |
| **In wt.%** | **With Shentou Ponded Ash** | **With Mongolia Fly Ash** |
| **$C_3S$** | ≈ 60 | 51.0 |
| **$C_2S$** | ≈ 0 | 0.1 |
| **$C_4A_3\bar{S}$** | 29.8 | 40.0 |
| **$C_4AF$** | 6.1 | 4.0 |
| **$C\bar{S}$** | 0.6 | 1.9 |
| **MgO** | 2.0 | 1.8 |

### 3.2. Results

X-ray diffractograms and Rietveld results from the samples made with both ashes fired at different temperatures are presented in Figure 7 and Table 4. For the clinker made with Mongolia fly ash, the low firing temperature of 1200°C was not high enough and some free lime (4.6 wt.%) was still present at the end of the clinkerization process. As a general rule, if the free lime content exceeds 2.0 wt.%, the clinkerization is thus considered not complete. However, the 1250°C firing temperature improved the clinker composition by decreasing the quantities of free lime (now at 1.4 wt.%) and belite, and increasing the amount of alite. When comparing the Rietveld data from Table 4 with the

theoretical values from Table 3, the amounts of calcium sulfoaluminate are very similar, with more than 30 wt.% for Shentou clinker, and around 40 wt.% for the Mongolia clinker, when fired at 1250°C. Regarding the amounts of belite and alite, the values are not close to the theoretical values, although when adding both belite and alite, totaling to 40 wt.% for the Shentou clinker and 60 wt.% for the Mongolia clinker, it is then close to the theoretical values. A higher firing temperature or a longer dwelling time would help by improving the formation of alite, although it may also decompose the calcium sulfoaluminate into tricalcium aluminate ($C_3A$).

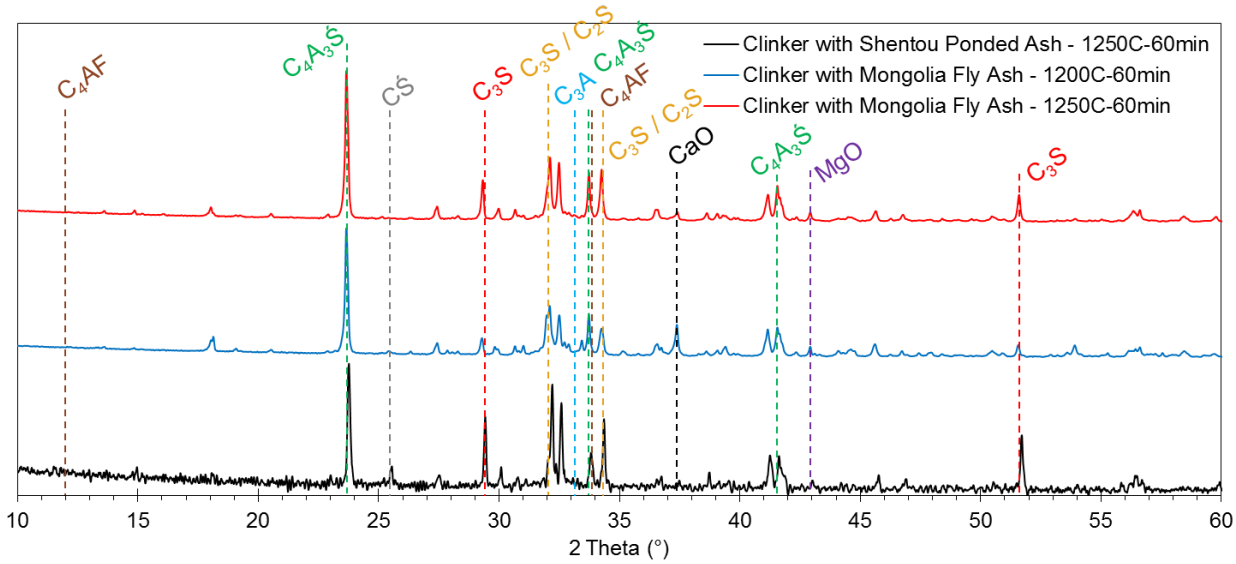


*Figure 7. X-ray diffractograms (XRD) of clinkers made with Shentou ponded ash and Mongolia fly ash fired at different temperatures.*

*Table 4. Rietveld analyses of clinkers made with Shentou ponded ash and Mongolia fly ash fired at different temperatures.*

| | With Shentou Ponded Ash | With Mongolia Fly Ash | |
|---|---|---|---|
| | **1250°C – 60min *** | **1200°C – 60min** | **1250°C – 60min** |
| **$C_3S$** | 40.2 | 12.3 | 29.3 |
| **$C_2S$** | 21.3 | 36.3 | 21.4 |
| **$C_4A_3Ś$** | 32.0 | 39.1 | 43.3 |
| **$C_4AF$** | 3.2 | 0.9 | 2.0 |
| **CŚ** | 2.0 | 0.6 | - |
| **MgO** | 1.2 | 1.7 | 1.2 |
| **$C_3A$** | - | 1.0 | 1.4 |
| **$f_{CaO}$** | - | 4.6 | 1.4 |
| **$C_{12}A_7$ (Mayenite)** | - | 3.6 | - |

* The sample with Shentou ponded ash was fired twice at 1250°C for 60 minutes

## CONCLUSION

The Shentou ponded ash and the Mongolia fly ash are both class F fly ashes and present similar chemical composition, with high amounts of aluminum oxide and silicon oxide, making them perfect candidates for use as raw materials for the production of OPC/CSA clinkers. The clinkers made from both ashes demonstrate that they can be successfully used to produce OPC/CSA hybrid clinkers. The next step of this project would be to produce large amounts of these clinkers and test the hydration processes and the mechanical properties of these cements.

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