Re-processing of Fly Ash and Coal to Produce Electricity and Cementitious Material

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Brief

Ash to Energy and Cement (ATEC) is a patented process for the treatment of high carbon coal fly ash, wherein fixed carbon in the fly ash is converted to thermal energy for steam or electrical power production where after, in a separate at high temperature reactor, calcium carbonate and other minerals are heated with the residual mineral components of the fly ash to form a hydraulically reactive material useful as a cement additive for producing high strength concrete. Recent studies have shown the promise of using the ATEC technology to process high ash, low rank coal directly into cement while generating excess power. Significantly, the ATEC process was used to replace up to 50% of ordinary portland cement (OPC) in concrete mixes with no loss in compressive strength while at the same time reducing the overall cost of the cement product.

ATEC Process Overview

In the ATEC process, high carbon coal fly ash and specific additives, including limestone, are re-processed at high temperatures, yielding a hydraulically active cementitious material that can be used in concrete mixes to replace up to 50% of the ordinary portland cement (OPC). ATEC technology enables beneficial use of an otherwise hazardous waste material to generate renewable energy, as well as a marketable special cementitious material (SCM), while reducing the adverse environmental impacts of both power generation and cement production. ATEC represents an economically viable means of remediating stored coal fly ash, much of which is not a candidate for current beneficial use in concrete mixes because of its high carbon content or oxide composition.

Coal Fly Ash

Coal fly ash (CFA) is a solid particulate by-product of coal combustion that can be removed from the flue gas stream by cyclonic separation, electrostatic precipitation and bag house filtration. CFA may contain environmentally harmful constituents, including a variety of heavy metals that can be emitted into the atmosphere or leach into the environment from wet or dry as impoundments.

Coal-fired power plants now employ methods for capturing the CFA from the flue gas stream using various techniques, including cyclonic separation, flue gas desulfurization units, electrostatic precipitation, and/or bag house filtration, among other techniques. The CFA is generally stored proximate to the coal power plants in wet or dry impoundments. Alternatively, the CFA is disposed in landfills.

Under appropriate conditions, CFA can be beneficially used as a supplemental cementitious material (SCM) in concrete mixes. CFA appropriate for use in concrete is comprised mainly of ceramic spheres (mainly silica and alumina). When used in concrete mixes, these pozzolanic materials can enhance the long-term quality, durability, and compressive strength of the resulting concrete.

In addition to the environmentally harmful components of CFA described above, coal-fired power plants generate sulfur and nitrogen oxide (SOx and NOx) emissions. If released into the environment, these oxides form weak acids upon contact with surface waters or precipitation. Power plant operators often use activated carbon to absorb SOx and NOx, as well as other acid gasses and toxic pollutants such as mercury, thus reducing harmful emissions in the flue gas stream.

The activated carbon used to absorb these pollutants increases the overall carbon content of the solid particulate material, including CFA that is recovered from the flue gas. United States Federal regulations prohibit using the CFA in cement and/or concrete mixes if the carbon content exceeds approximately 6%, as determined by loss of weight upon ignition (>6% LOI).

One reason that the high carbon CFA cannot be used in concrete is that the carbon interferes with air entrainment (the intentional creation of tiny air bubbles in concrete), introduced to increase the durability of hardened concrete. Thus, the activated carbon used to clean the flue gas may render the recovered CFA unusable as supplemental cementitious material. This, in turn, can result in more CFA being stored at dry landfills or in wet slurry impoundments.

Accumulations of coal fly ash and associated bottom ash and boiler slags in landfills and wet impoundments constitute a substantial environmental hazard. These impoundments can fail, causing billions of dollars of damage in the process. In addition, toxic components of the CFA may leach into ground water when the CFA is stored in unlined impoundments. The ponds and impoundments where much of the CFA is stored by the operators of coal fed power plants are of increasing environmental concern worldwide.

Low Rank Coals

In many regions, there are abundant reserves of low rank coals, such as lignite. With relatively high ash and moisture content, this coal is a marginal fuel for electrical generation. With ash contents as high as 45%, large ash disposal areas are required for a relatively low amount of power generated. High moisture contents also require drying or reduce the efficiency of thermal conversion. Additionally, the low energy density makes long distance transportation uneconomical.

The high ash content that represents an economic and environmental obstacle to the use of lignite for power generation, can be an advantage when applying the ATEC process. Our laboratory and modeling studies have shown that cement can be produced directly from a mixture of lignite and limestone, while producing excess power. By combining the cement making and power generation processes, the overall environmental impact is greatly reduced versus producing cement and power separately.

Cement Production

Cement production is an important source of both greenhouse gases and heavy metal emissions. Portland cement production in the United States is responsible for releasing 90 million tons of carbon dioxide into the atmosphere annually. This represents over a ton of carbon dioxide per ton of cement produced. Cement production is also a major source of heavy metal emissions. It is widely known that typical replacement of cement with usable fly ash currently reduces millions of tons of carbon dioxide emissions by reducing the need for production of portland cement.

Gasification of High Carbon CFA and Lignite

Gasification is a process wherein organic carbonaceous materials are dissociated at high temperatures in an oxygen-starved environment to form a gas known as gas phase fuel known as synthesis gas (syngas), or producer gas, depending on the relative nitrogen content. The producer gas generated in the ATEC process will be referred to as fuel gas and is comprised mainly of nitrogen, carbon dioxide, carbon monoxide, hydrogen, methane and water vapor, as well as trace amounts of sulfur and other oxides. **Figure 1** shows the principal components in the ATEC process.

In the gasification process, as depicted in **Figure 1**, the first rotary kiln thermal reactor is pre-heated to approximately 1300^{o} F prior to the introduction of the fuel and mineral mixture, as indicated by ultimate and proximate analysis of the materials being processed.

A portion of the fixed carbon in the mixture is converted to fuel gas in the first reactor. This gas is cleaned in a cyclone and combusted to produce steam in a heat recovery steam generator (HRSG). The steam can be used for industrial processes or to generate electricity. The remaining ash and unreacted carbon are then transferred to a second rotary kiln wherein the temperature is increased to approximately 2,500^{o}F. At this temperature any remaining fixed carbon is converted to fuel gas and the inorganic material remaining is partially fused or sintered forming a clinker.

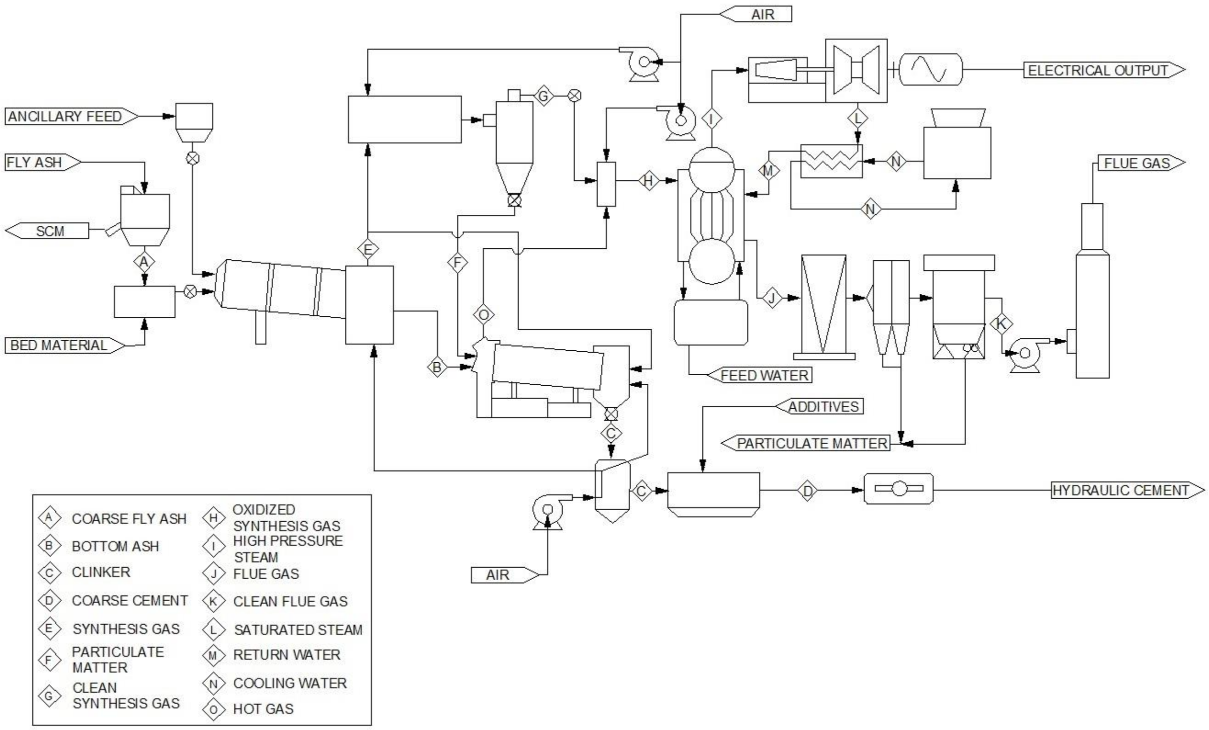


Figure 1. *Process diagram showing the process feed system, first rotary kiln gasifier, the high temperature rotary kiln and clinker cooling and grinding equipment, as well as the fuel gas combustor, cyclone, boiler and steam power plant*

The cooled clinker possesses hydraulic cementitious activity similar to that of ordinary portland cement (see image of product). Depending on the market in the area, the feed mixture can be adjusted to produce an ordinary portland cement, with narrow quality requirements defined by ASTM, or a supplemental cementitious material. A supplementary cementitious material produced by the ATEC process, was used to replace up to 50% of ordinary portland cement in concrete mixes with no loss in compressive strength, even at low setting times. In standard ASTM testing using a 20% replacement with ATEC cementious material, the compressive strength of concrete was increased at 7, 14 and 35 days after casting, as compared to the analogous portland cement only mix.

Provided there is sufficient carbon in the feedstock, the gasification process will remain auto-thermal. That is, no ancillary fuel, such as additional coal or natural gas, would be required to maintain the temperatures needed to form the cementitious material. Excess heat available for power production also depends on carbon content. **Table 2** below shows an example of calculated inputs and outputs per 200 tons of material processed.

Table 2. Feed Mixture and Output for a planned 200 ton per day ATEC Plant using Lignite

Feed Mixture		**Unit**
Lignite	50.2	tons/day
Ash	12.8	tons/day
Limestone	135.4	tons/day
Output		
Thermal Power	5.1	MW
Cement Clinker	112.3	tons/day

ATEC Application Examples

Laboratory and modeling studies have shown the feasibility of the ATEC process using a variety of feedstocks. Early testing focused on high carbon fly ash, which is especially abundant in regions of the United States. More recently testing has been focused on using low rank Turkish coal as a feedstock, which happens to have a similar heating value as the high carbon fly ashes used previously.

High Carbon Fly Ash

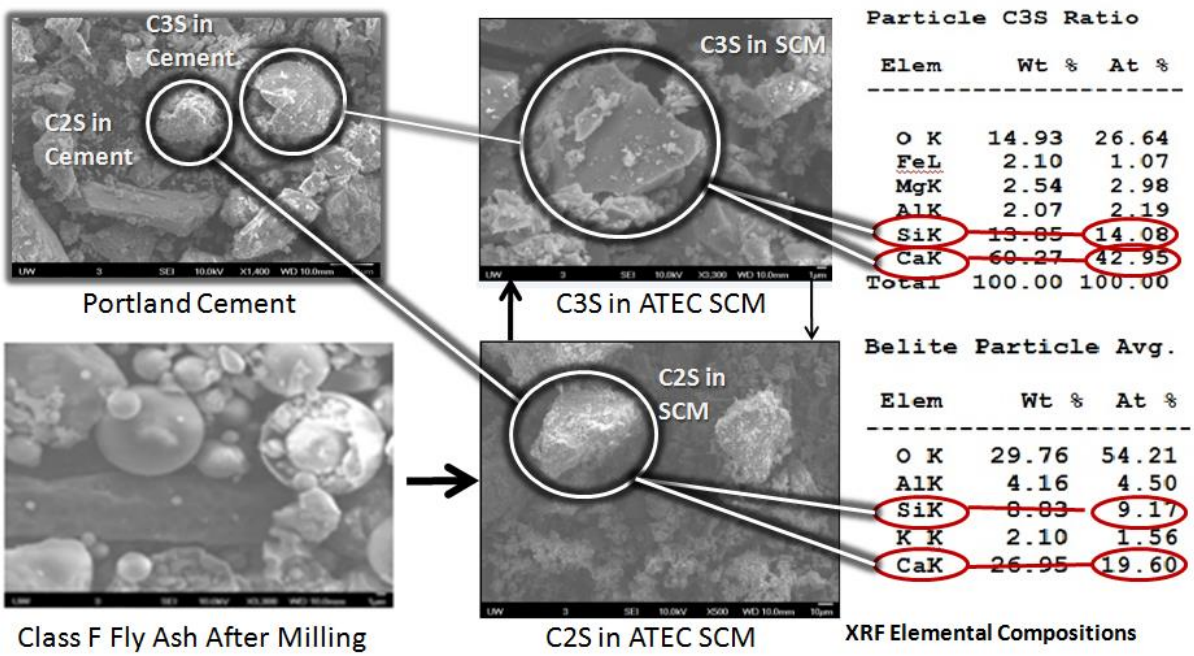
Class C coal fly ash having a carbon content in excess of 30%, as determined by loss on ignition (“LOI”), and an average calorific value of approximately 5,000 BTU/lb was used to produce a hydraulically reactive cementitious material that imparts high strength characteristics to the concrete from mixes in which it is used. The coal fly ash used was from a variety of the coal fired power plants operated by the Tennessee Valley Authority (TVA). But because of the high carbon content, the fly ash is unsuitable for use as an SCM in concrete mixtures.

Figure 2 below shows the elemental compositions, as determined by x-ray fluorescence spectrometry (XRF) of the re-processed coal fly ash from the TVA plant located in Kingston, TN The XRF results shows coal fly ash derived ATEC product as compared to elemental composition of the analogous particles in Portland cement. The structure of the fly ash has been substantially changed by ATEC re-processing. Specifically, the cenospheres, as shown in **Figure 2**, have been broken down and no carbon was detected.

Atom percent, as determined by XRF elemental compositions of specific particles in the ATEC material, showed the typical compositions for C2S (belite) and C3S (alite), the specific calcium silicate mineral components of portland cement.

Figure 2 *Electron micrographs and XRF elemental composition data from portland cement and from*

- SEM images of portland cement, milled fly ash, and the tricalcium silicate (C3S) and dicalcium silicate (C2S) products made from this fly ash by the ATEC process. Elemental compositions by XRF confirm the presence of these reactive cement components.



ATEC cementitious material made from Kingston, TN ponded fly ash

While the ATEC cementitious material product may be cast to mortar samples without the addition of portland cement, the best compressive strength test results were obtained when approximately 20 -25% of the portland cement in a standard ASTM mix was replaced with the ATEC material.

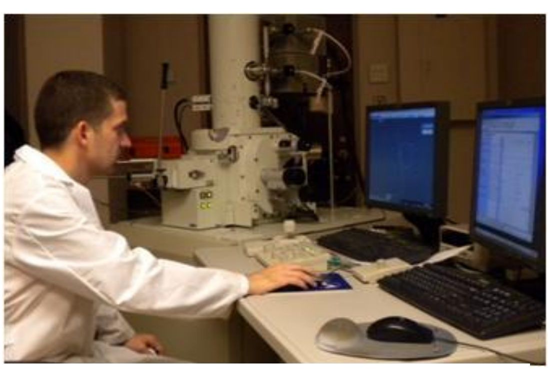


***Figure 3**. Scanning electron microscope with EDAX XRF for determination of particle elemental compositions*

Table 3 below compares the compressive strength data for concrete having a mixture of the ATEC reprocessed fly ash compared to a sample of 100% Portland cement at 7 days and at 35 days after casting. The ATEC reprocessed fly ash (cementitious product) sample is was made with a 20% fly ash replacement for the portland cement that is normally used in an ASTM mixture. The high relative strength of the fly ash mixture after both 7 and 35 days shows the hydraulic activity of the coal fly ash under compression testing performed in accordance with ASTM standard 109C (see icon image on Page 1.)

Table 3 Comparison of compressive strengths at 7 and 35 days for ATEC and 3 other coal fly ash materials replacing 20% of the portland cement in ASTM concrete mixes and showing that the highest compressive strength was achieved using the ATEC replacement material

		7 days		35 days	
% Replacement in Concrete Mix	**Process**	**Compressive Strength (psi)**	**SAI***	**Compressive Strength (psi)**	**SAI**
20	**ATEC**	**7338**	**106**	**9705**	**105**
100	Portland Cement	6923	100	9240	100
20	Fly Ash As Received	6350	92	7976	86
20	Carbon Burnout	5835	84	7866	85
20	Carbon Burnout w/ Coal	6078	88	7632	83

*Strength Activiy Index, or the compressive strength of the concrete with portland cement normalized to 100

Turkish Coal

Testing with Turkish coal included both a laboratory testing phase and a modeling phase. Both were reviewed by a third party engineering firm. The purpose of the studies was to determine the feasibility of producing ordinary portland cement using the ATEC process and designing a small scale facility to be built at a specific location Turkey. Using lignite, fly ash, and limestone available in the region, the laboratory work showed that these materials can be processed successfully in the two-stage ATEC process to produce cementitious clinker. Information valuable for the design of the future plant was obtained, such as residence times and refractory requirements. Larger scale laboratory tests are required to produce enough material for compression testing of the resulting cement.

Modeling of the ATEC process using Turkish lignite was conducted in collaboration with Reactive Engineering International, USA (REI). REI has special expertise in modelling both cement kiln technology as well as combustion systems, making them uniquely qualified to evaluate, and advise the design of a functioning ATEC system. Information provided by REI led to a significant reimagining of certain aspects of the system including the optimal mixture of the feed materials, material handling, and size of equipment. The result of the modelling study was a first level design of a 200 TPD facility to produce portland cement and excess power from lignite and limestone. This design includes site layouts, price estimates, emission estimates, and equipment specifications.

***Figure 4**. Clinker created from Turkish lignite and limestone. Scale bar represents 5 cm.*

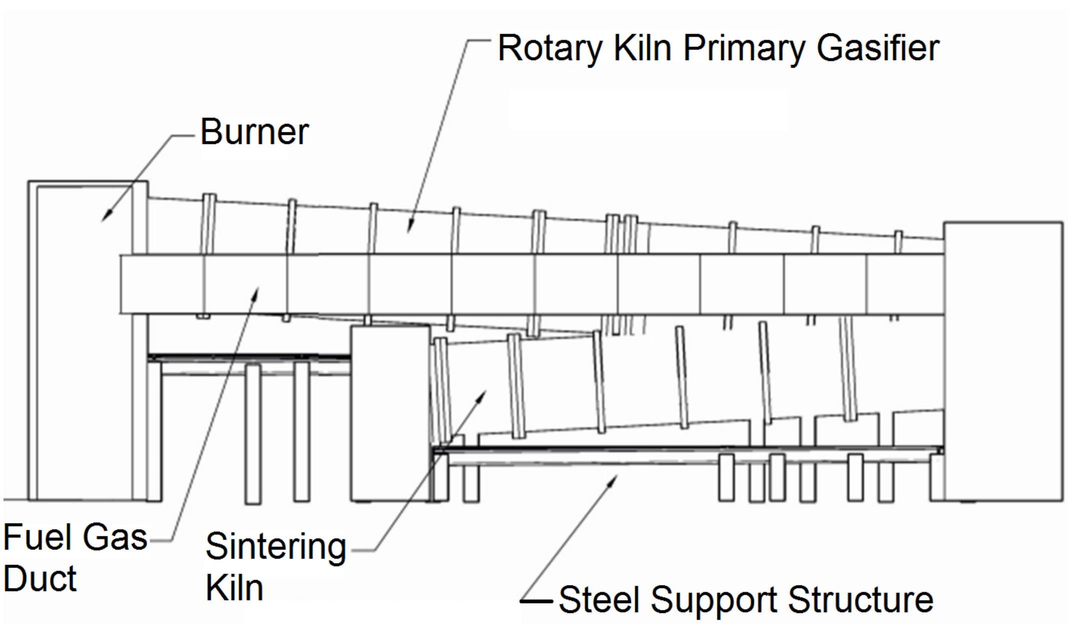


***Figure 5.** Elevation drawing of some of the core equipment for a 200 TPD system producing ordinary portland cement.*

Environmental and Economic Advantages of the ATEC Process

Environmental benefits of the ATEC process are substantial. Foremost among these is the fact that it converts a potentially hazardous material to a safe and beneficial article of commerce.

In contrast to many of the other fly ash beneficial use schemes, ATEC works best with many of the fly ashes least desirable for use in concrete. These include high-carbon, variable carbon, high-calcium, large particle, and previously ponded fly ashes.

The fact that ATEC can use long-stored fly ash from landfills means that, even long after coal power plants close, the ATEC process could be used to remediate waste that would otherwise be in the ground indefinitely. By converting the ash from landfills or slurry ponds, ATEC can help in the remediation of these sites. Such remediation eliminates the potential for regulated constituents including toxic metals that can leach out of fly ash and enter the environment. Research has shown that heavy metals, including mercury, are best sequestered in concrete, where their release into the environment is not greater than from many naturally occurring rock substrates.

Beyond the environmental benefits of fly ash remediation, are the benefits of replacing a portion of the portland cement used in concrete. Our models indicate that, pound per pound, the ATEC process reduces carbon dioxide emissions by approximately 4% as compared with conventional portland cement production. ATEC cement also requires much less limestone and no clay, materials that need to be mined for cement production reducing the cost of the end-product. Unlike several technologies under development that totally replace concrete, ATEC compliments current concrete technology by reducing its environmental impact.

The ATEC process also has an economic benefit. Due to sale of power, the process can operate at a profit at scales as small as 200 TPD. A 200 TPD facility would produce approximately 2 MW that could be sold to the power grid. Besides profits for the operator, an ATEC system also provides a lower cost alternative to utility companies that would otherwise have to pay to have fly ash dumped in lined landfills. With government regulation of fly ash disposal increasing, the price of fly ash disposal is likely to increase. As more stringent environmental regulations make power generation by coal-fired plants more expensive, relative cost of ATEC processing will be offset to a greater extent by the increased cost of fly ash disposal.

Electricity generated by the ATEC process releases over 90% less SOx, NOx, and particulates matter per kilowatt-hour than the coal fired plants that originally produced the fly ash. Besides providing a source of clean energy, the sale of power helps offset the costs of processing and allows ATEC to be an economically viable, free-market solution to coal ash related environmental concerns.

Status of ATEC Process Development

Much of the science and engineering work required to apply the ATEC process has already been completed. Lab tests and computer models have confirmed the technical feasibility of using the specific materials to produce portland cement. A detailed heat and material balance is complete and has been used to size equipment, ducts, and estimate parasitic loads and emissions.

Business Potential

The worldwide market for Ordinary Portland Cement (OPC) products is not only sound but projected to grow at rate of approximately 4.5% annually through 2019 to 5.2 billion metric tons[1] per year. Therefore, from strictly a financial aspect, this project represents a strong business case. Not only does the OPC product enjoy the advantage of having an inelastic high demand curve but the process itself provides for additional potential revenue streams in the form of electricity/steam generation, as well as coal ash clean up. Equally important is the fact that patents on this technology controlled by one of an EnviroPower partners virtually eliminates competition.

Lastly, laboratory testing of the ATEC technology at the University of Washington has validated this process and as well as the quality of the laboratory generated clinker products. These successful results indicate that the project is now ready for the next step of development.

[1] Source: The Concrete Producer magazine, December 2015 Issue