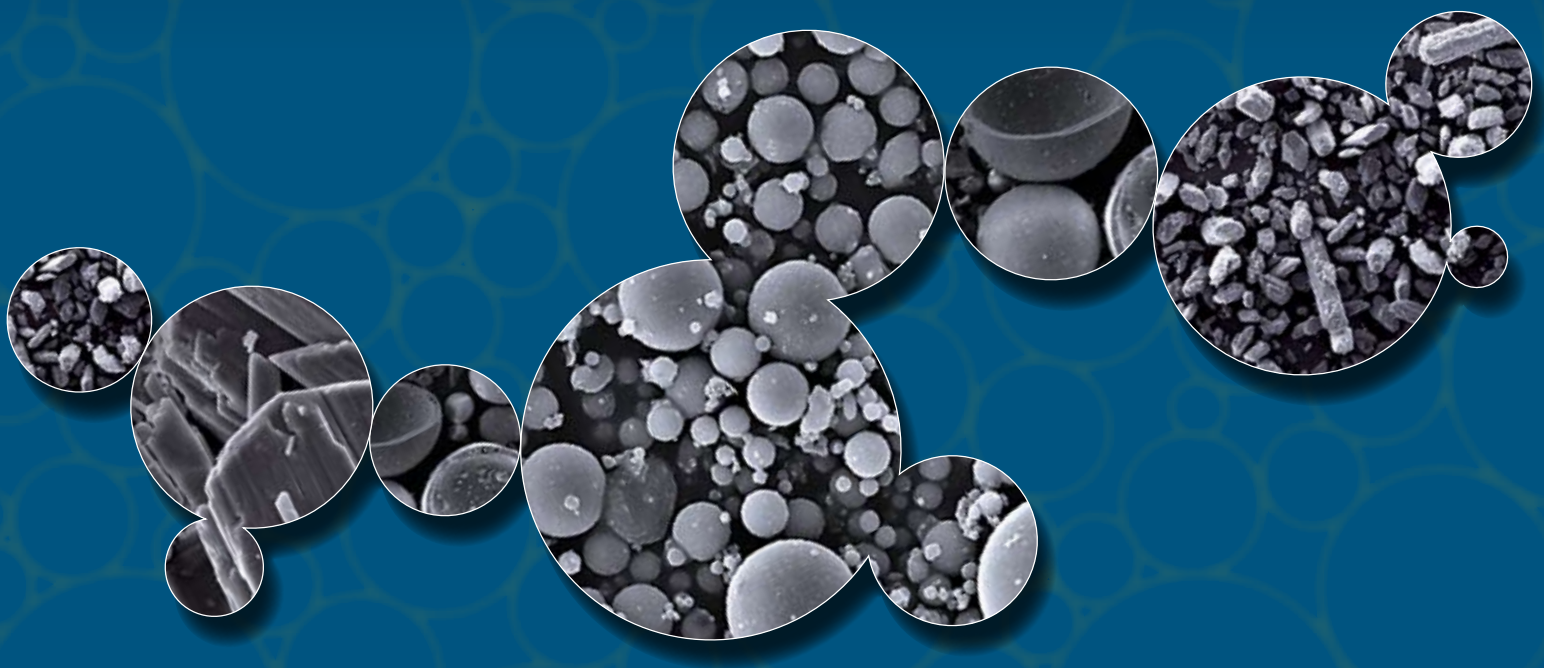
# coal combustion and gasification products



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## Coal Combustion & Gasification Products – the journal

Welcome to the second CCGP insert in ACAA's Ash-at-Work. You will find abstracts of the papers published during 2010-2011 in the online journal, ***Coal Combustion and Gasification Products*** (www.coalcgp-journal.org). The ***CCGP Journal*** is a science and engineering journal devoted to the sustainable production and utilization of an economic resource and the environmentally-sound disposal of the portion of the material that cannot, at least for now, be utilized. It is collaboratively published by the American Coal Ash Association and the University of Kentucky, Center for Applied Energy Research. Allen Press, a respected publisher of scientific journals, provides the electronic submission portal and manuscript processing services. Together we pledge the following:

- First, this journal is carefully reviewed and judicated by academic and industrial experts. We strive to publish papers of the highest quality and that meet the highest scientific standards. What you will find will be reliable, honestly presented, and worth reading.

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- Third, we keep it relevant. By adding a print version of the journal consisting of abstracts of the online journal and other relevant materials to *Ash at Work*, the premier trade magazine published by ACAA, we will provide readable synopses of current research to all stakeholders.

*Coal Combustion and Gasification Products* fills an underserved niche in the literature as a high-quality refereed journal. To this end, we have assembled a knowledgeable and experienced editorial board to serve as our first line of paper reviewers. In addition, we will continue to reach out to the broader community of ash scientists and engineers to review papers. The success of the journal depends on all of us: authors, reviewers, readers, and the editorial staff at the CAER.

We invite you to browse the following pages and to read the full-text papers from the journal web site: www.coalcgp-journal.org.

Feel free to contact us with ideas on ways this journal can assist our shared industry.

On behalf of UK CAER and ACAA
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## Phaselous vulgaris Growth under the Influence of Manufactured Coal Ash Aggregates

Sangchul Hwang, Imiraily Hernandez, Isomar Latorre, Sahid Rosado, *Department of Civil Engineering, University of Puerto Rico.*

Manufactured coal ash aggregates (MAs) are a 2:1 (w/w) solidified composite of fly and bottom ash. The current study assessed the feasibility of beneficial utilization of MAs as a subsoil substitute for open-pit restoration to phyto-viable land. A series of indoor and outdoor experiments examined Phaselous vulgaris growth under the influence of MAs in the soil environment.

With the MAs layer below the topsoil, P. vulgaris showed enhanced growth with respect to shoot height, leaf number, and leaf chlorophyll intensity. Similar growth enhancement was observed when the MAs were mixed with topsoil or applied as a micronutrient source over the topsoil. Thus, MAs are beneficial as a subsoil substitute for open-pit restoration to phyto-viable land, reducing exploitation of natural soil resources and enhancing plant growth.

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## Enriched Coal Ash Utilization for Augmenting Production of Rice under Acid Lateritic Soil

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The use of industrial wastes such as fly ash (FA) or rice husk ash (RHA), along with paper factory sludge (PFS), farmyard manure (FYM), and chemical fertilizers (CF), under integrated nutrient management, was studied in acid lateritic soil on rice. Application of combined fertilization sources increased growth, yield attributes, and yield (up to 92.3 and 9.7% over control and CF, respectively) of wet season rice. The uptake of N, P, K, Ca, Mg, Fe, Mn, Zn, Cu, and Co was increased under combined fertilization sources. The study also indicated that such integrated plant nutrition system improved physico-chemical properties of soil with respect to bulk density, pH, electrical conductivity, organic carbon, and available nutrient content.

Utilization of these wastes saved chemical fertilizers to the extent of 37.8, 59.7, and 86.5% N, P, and K respectively, with an added advantage of minimizing environmental pollution.

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## Mineralogy and Leaching Characteristics of Coal Ash from a Major Brazilian Power Plant

Luis F.O. Silva, Marcos L.S. Oliveira, *Catarinense Institute of Environmental Research and Human Development, Brazil.* Colin R. Ward, Zhongsheng Li, *University of New South Wales, Australia.* James C. Hower, *University of Kentucky Center for Applied Energy Research.* Maria Izquierdo, Xavier Querol, *Institute of Environmental Assessment and Water Research, Spain.* Frans Waanders, *North West University, South Africa.* Rachel S. Hatch, *University of Kentucky Department of Earth and Environmental Sciences.*

The feed coals, fly ashes and bottom ashes collected from seven different units in a major Brazilian PF power plant have been subjected to comprehensive mineralogical, geochemical, and petrographic studies, to investigate the links between feed coal and ash characteristics. Ashes from two of the units were collected while the coal was being co-fired with oil as part of the boiler start-up procedure, allowing the impact of oil co-firing on ash characteristics also to be evaluated. High proportions of unburnt carbon and high proportions of retained sulphur were found in the fly ashes produced during oil co-firing, probably reflecting less efficient combustion and associated lower combustion temperatures. Higher concentrations of a number of relatively volatile trace elements were also noted in these fly ashes, compared to the fly ashes collected from units under normal operating conditions.

The fly ashes produced during oil co-firing gave rise to acid pH conditions in water-based leaching tests, in contrast to the alkaline pH associated with fly ashes produced during normal operations. This probably reflects higher SO3 contents relative to total CaO + MgO for the co-fired ash samples. Many trace elements that are typically mobilised as cations were also more abundant in leachates from the co-fired fly ashes. This is due, most likely, to the more acid pH conditions involved. Despite similar or even higher total concentrations, however, elements that are typically released from coal ash as oxy-anions were less mobile from the co-fired fly ashes than from the normally-fired fly ash materials.

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## Fullerenes and Metallofullerenes in Coal-Fired Stoker Fly Ash

Luis F.O. Silva, Ka′tia DaBoit, *Catarinense Institute of Environmental Research and Human Development, Brazil.* Carmen Serra, *Universidade de Vigo, Spain.* Sarah M. Mardon, *Kentucky Department for Natural Resources, Division of Abandoned Mine Lands.* James C. Hower, *University of Kentucky, Center for Applied Energy Research.*

A suite of high-As, high-C fly ashes from a university-based stoker-fired coal boiler were analyzed by a number of techniques, including high-resolution transmission electron microscopy (HR-TEM), time-of-flight secondary ion mass spectrometry (TOFSIMS), X-ray

photoelectron spectroscopy (XPS), and field-emission scanning electron microscopy (FE-SEM). The sooty carbon is in the form of nano balls with the major fullerenes at C60 +, C70 +, and C80 +, with species at C2 increments from C56 + to C78 +.

Arsenic and Hg, among other metals, are found in association with the fullerenes, but, with our techniques, it is not possible to determine if the metals are encapsulated by the fullerenes or attached to the side of the structure. TOF-SIMS studies suggest an association of As with the Al-Si glass; an association of Pb with oxides, sulfates, and carbon; Hg with carbon; Se in elemental form with carbon; and Cr in a variety of forms, including nano carbons, Fe sulfates and oxides, glass, and Cr-oxyhydroxides.

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## Impact of Manufactured Coal Ash Aggregates on Water Quality during Open Pit Restoration: 1. A Statistical Screening Test

**Sangchul Hwang, Isomar Latorre,** *Department of Civil Engineering, University of Puerto Rico.*

Utilization of manufactured coal ash aggregates (MAs) as a subsoil substitute during restoration of an open pit was assessed in a three-factor, two-level factorial analysis. The factors of interest were the MA application rate (2:1 or 1:2 topsoil/MA volume ratio), rainfall intensity (high or low), and aggregate size (2.36–4.75 mm or 4.75–9.53 mm). Among the water quality parameters examined (pH, turbidity, heavy metal content (lead and cadmium), conductivity, and hardness), the last two parameters were significantly higher (p,0.05) in soil amended with MAs than in a control reactor using sand. A low rainfall intensity and larger aggregate size resulted in a lower water quality with regard to conductivity (7,12 mS/cm) and hardness (600,2000 mg/L as CaCO3) during the 63 day experiment.

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## Trace Element Partitioning and Leaching in Solids Derived from Gasification of Australian Coals

**Alexander Ilyushechkin, Daniel Roberts, David Harris, Kenneth Riley,** *CSIRO Energy Technology, Australia.*

Trace element concentrations vary between coals from ppb to ppm levels and can depend on the rank of the coal and its geological origins. During gasification, some of the trace elements are volatilised at high temperatures and may condense and deposit in cooler downstream parts of the system or in quench water streams. Some species may appear in condensed phases such as slag or fly ash. Changes in the trace element concentrations in the slag and fly ash from that of the parent coal are expected due to the reactions occurring at high temperatures and the different chemical activity of the trace element phases in the slag, fly ash, and syngas. Four Australian coals were used in an entrained flow gasification test program conducted in the Siemens 5 MWth gasification test facility. Solid samples were collected from different points in the gasification process during each test.

Compositions of these samples were analyzed and the distribution of trace elements was studied.
The elements can be classified as follows, according to their tendency to appear in the slag and fly ash:

- Partitioned between slag and fly ash: Cu, W, Mo, Cd, Bi, Zn, Sn, Sb
- Partially volatile and depleted from either slag or fly ash: Be, Th, Sc, Y, Li, Mn, Ni, Sr, Ba
- Highly volatile (i.e. were not observed in either slag or fly ash): As, Se, B, Hg, F, Pb, V.

Comparison of these experimental results with equilibrium calculations of trace element appearance in the condensed phases suggests that the modelling approach is suitable only for certain elements. For several of the trace elements of significance in this study, kinetic factors have to be considered in conjunction with thermodynamic modelling. The leaching behaviour of the trace elements in the slag was also studied. This work shows very low leachability for most of the trace elements except Zn and Sb, which, due to their relatively high volatility, reported to the slag samples in very low concentrations.

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## Co-Disposal of Dry FGD By-product with Coal Gasification Ash and Inorganic Brines

**Jabulani S. Mahlaba, P.C. Pretorius, M.P. Augustyn,** *SASOL Technology (Pty) Ltd, South Africa.* **Subal Maharajh,** *SASOL Technology (PTY) Ltd, South Africa.*

There is a growing pressure from the environmental authorities and public bodies to reduce anthropogenic pollution. Stringent environmental legislation is being implemented for industries around the world, even more so for coal consuming industries. Control of gaseous emissions is one of the areas that are receiving considerable attention towards sustainable development. Coal combustion in coal-fired power utilities emits SOx to the atmosphere.

Flue gas desulphurisation (FGD) is a well known technology often used to mitigate sulphur emissions in coal-fired power utilities. Dry FGD technology traditionally uses lime to neutralise SOx, and forms a mixture of anhydrite (CaSO4), and calcium sulphite (CaSO3). It is apparent that scrubbing of SOx from the air converts an atmospheric problem into a solid form requiring acceptable fate. Several options are reported in literature such as utilisation in agriculture, cement and concrete manufacturing, and wallboards. A feasibility study for the implementation of a dry FGD technology is presented.

This paper reports the preliminary findings of the option where FGD by-product is co-disposed with coarse ash and brine;

assuming that quantities of FGD by-product exceed utilisation demand. Coarse ash is defined as the combination of gasification ash and bottom ash in a 4:1 ratio. The study examined the influence of moisture content, chemistry of the liquid medium, and ratio of FGD by-product to coarse ash on the physical and chemical properties of the cured mix. The results demonstrate that the chemistry of raw materials influences the final properties of the resultant product. Based on the preliminary results co-disposal of coarse ash, excess FGD by-product, and brines will potentially present an environmentally less harmful option in a single site.

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## Compositional Variations in Pilot Gasifier and Laboratory-Produced Slags and their Impacts on Slag Viscosity and Coal Assessment

**Alexander Ilyushechkin, Daniel Roberts, David Harris,** *CSIRO Energy Technology, Australia.*

The flow behaviour of coal mineral matter at high temperatures is an important parameter for coal use in entrained-flow gasification technologies. Recently, gasification performance data was obtained from a series of pilot-scale gasification tests on a suite of well-characterised Australian black coals. Evaluation of the results of the pilot tests and the detailed laboratory investigations provided the opportunity for evaluation of the practical applicability of different laboratory and modeling techniques for coal assessment in terms of mineral matter behaviour in entrained flow gasification.

A series of viscosity measurements was made over the range 1200–1600uC using slags produced in a pilot scale gasifier at temperatures between 1200 and 1700 uC, and laboratory-produced slags. These data were compared with viscosity predictions based on an empirical model developed from an extensive database of slag viscosity measurements. Major differences between predicted and measured viscosities were investigated and, where appropriate, related to slag composition and microstructure.

There were some significant differences (in some cases up to 100% of the viscosity values) in the viscosity behaviour of laboratory-prepared slags and those produced during the pilot-scale gasification test runs. These differences were attributable to differences between the composition of the laboratory-produced slags and those tapped from the pilot scale gasifier. The major source of these compositional variations appears to be a result of partitioning of mineral matter components into fly ash and slag in the gasifier, and the possible subsequent interaction of this slag with slag already present on the wall of the gasifier.

These observations have implications for the manner in which coal mineral matter is assessed for its likely behaviour, and ultimate suitability for use, in entrained flow gasification systems. In order to improve the reliability of coal slag assessment procedures, test procedures should include preliminary modeling based on expected coal ash and slag compositions, viscosity measurements of laboratory-produced slags, and analyses of ash and slag compositions where possible to ascertain the degree of compositional partitioning and its impact on slag behaviour.

Ongoing work is required to better understand the nature of mineral matter transformations under gasification conditions and the impact of this on coal and gasifier performance.

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## The Leachability of Major Elements at Different Stages of Weathering in Dry Disposed Coal Fly Ash

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Large quantities of solid residue are generated by coal-fired power stations in many parts of the World. The disposal and management of the unused fly ash remains a major problem to the environment. The weathered dry disposed ash cores comprise of major element constituents such as Al, Si, Ca, Mg, Fe, Mn, Na+ and K+. The mobility patterns and mineralogical associations of major elements in weathered dry disposed ash dumps aged 1-year-old, 8-year-old and 20-year-old from a coalfired power station in South Africa were investigated using a modified sequential extraction scheme. The extraction sequence was as follows: (1) water soluble, (2) exchangeable, (3) carbonate, (4) Fe and Mn and (5) residual. A total acid digestion was carried out on the original sample prior to extraction to validate the extraction procedure. The distribution of Si, Fe, Mn, Ca, Mg, Na+, and K+ in 59 drilled ash core samples was determined by inductively coupled plasma mass spectrometry.

The leachability of the seven elements from different fractions proved to be different; so various distribution patterns have been achieved. The highest concentration of analytes is recorded in the water soluble, exchangeable, and carbonates of 1-year-old ash cores hence it is the least leached. The concentration of each element in each fraction was calculated as a percentage of the total metal content for the 1-year-old ash cores. The average amount of the major elements in the easily soluble fractions of 1-year-old ash core samples are: water soluble: Na (21%) . Ca (10.2%) . Mn (8.4%) . Si (4.0%) . K (2.58%) . Mg (0.05%) . Al (0.003%) . Fe (0.001%), exchangeable: Ca (37.04%) . Mg (12.6%) . Na (11.26%) . Mn (10.3%) . K (3.17%) . Si (1.6%) . Al (0.27%) . Fe (0.33%), carbonate: Mn (41.21%) . Ca (37.9%) . Mg (32.9%) . Al (29.25%) . Si (25.39%) . Fe (21.39%) . Na (2.6%) . K (2.23%).

The mobility of major elements in the weathered ash dumps are influenced by heterogeneity in the ash dump, inhomogeneous continuous brine irrigation and chemical interaction of ash cores with ingressed CO2 from atmosphere and percolating rain water.

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## Zinc Speciation in Power Plant Burning Mixtures of Coal and Tires

Luis F.O. Silva, *Catarinense Institute of Environmental Research and Human Development, Brazil.* Marcos L.S. Oliveira, *Catarinense Institute of Environmental Research and Human Development, Brazil.* Carmen Serra, *Universidade de Vigo, Spain.* James C. Hower, *University of Kentucky Center for Applied Energy Research.*

Fly ash from the cyclone-boiler co-combustion of high-S, high volatile bituminous coal and tire-derived fuel (tdf) was studied using a variety of chemical, optical, and microbeam techniques. Fly ash, dominated by Al-Si glass with lesser amounts of coalderived carbons, Fe-spinels, and tire-derived carbons, has Zn concentrations ranging from 2200 ppm (1st ESP row) to 6900 ppm Zn (3rd ESP row). Zinc occurs in Zn-rich nanoparticles in the Al-Si glass phases and as ZnO in amorphous and crystalline nanominerals, Fe- and Zn-sulfides, Pb-Al-Fe sulfates, and Zn sulfates. Iron-rich, Al- and Ti-bearing spinels contain accessory Zn2+, Cr3+, Mn2+, and Pb2+. Fe-sulfates and phosphates nanoparticles incorporate As, Cr, V, Ni, and Zn. Fullerenes were not detected in this fly ash, potentially due to the higher temperature of combustion in the cyclone boiler. Zinc was detected by XPS, but the low binding energies mitigated against the determination of the speciation of the element.

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## A Multi-Analytical Approach to Understand the Chemistry of Fe-Minerals in Feed Coals and Ashes

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Seven feed coals used in the Brazilian power generation industry were obtained and subsequently analysed together with fly ash and bottom ash from a major Brazilian power plant. The samples were investigated by means of room temperature Fe-Mo¨ssbauer analyses, X-ray diffraction, Raman spectroscopy, scanning electron microscope and petrographic analysis. In addition, nanometer-sized crystalline phases in coals and ashes were characterized using an energy-dispersive X-ray spectrometer and a high-resolution transmission electron microscope. The major identified Fe-bearing minerals in the coals were found to be actinolite, ankerite, chalcopyrite, chlorite, goethite, illite, ilmenite, magnesioferrite, natrojarosite, pyrite, pyrrhotite, and siderite; whilst in the fly ash and bottom ash, ankerite, chlorite, chromite, goethite, hematite, hercynite, jarosite, maghemite, magnesioferrite, and magnetite were identified. Most of the Fe in the ash samples was present as Fe3+ resulting from the melting of Fe and silicates during combustion. The fraction of glassy Fe in those particles is high because of the high contact probability between Fe melt and silicates. The combination of the various methods offers a powerful analytical technique in the study of coal and coal ashes. This investigation can be regarded as an introductory and prospective study prior to further quantification.

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## Geochemical Controls of Coal Fly Ash Leachate pH

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When coal fly ash is initially mixed with water, the initial pH of resulting extract or leachate may be strongly acidic (4) or alkaline (12). With time, however, this pH range tends to narrow because of geochemical buffering reactions. Because pH is the major variable that controls the leaching of many potential groundwater contaminants, understanding the long-term pH behavior of fly ash leachate is crucial to evaluating the environmental impacts of fly ash management. Using laboratory extract data, kinetic-geochemical models were created to gain a better understanding of the potential buffering that influences the long-term pH of ash leachate.

We used the kinetic software REACT which is a part of the software Geochemist's Workbench, Release 7.0.5 with the thermodynamic database thermo.com.v8.r6+. For this investigation, two fly ash samples were chosen. An alkaline fly ash sample was selected for this study to initially help validate the application of model. Then the leaching of an acidic fly ash sample was modeled. These specific ash samples were selected because appeared to be reasonably representative of an alkaline and acidic fly ash. These samples were also selected because of the availability of time-dependent leaching data to compare with the kinetic models, and detailed mineralogical and chemical characterization to use as a basis for constructing ash models.

The initial acidity observed in the laboratory studies was matched by using sulfuric acid and pyrite as reactants in the kinetic model. The initially low pH of acidic fly ashes was short-lived because the acidity was neutralized by the dissolution of calcium and magnesium oxides, then buffered by carbon dioxide yielding a pH of 7 to 8. Alkaline fly ash leachate (pH > 10) tends to absorb carbon dioxide, and the resulting pH of the liquid phase decreased with time to a pH between 8 and 9. Kinetic modeling suggests that the chemical composition of short-term laboratory extracts of coal fly ash will not be representative of long-term leachate after equilibrating with the atmosphere. The rate of change in pH, however, was accelerated in the laboratory studies because the slurries were well mixed. Under field conditions, the impacts of passive carbonate buffering would likely require longer periods of time. It appears that kinetic models such as REACT can be used to estimate the pH of leachate from coal combustion products for time frames that are not practical under laboratory conditions. Additional research is needed, particularly using field-scale data.

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## Effect of Additive on the Performance Characteristics of Centrifugal and Progressive Cavity Slurry Pumps with High Concentration Fly Ash Slurries

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Slurry pumps that are used in the hydraulic transportation of fly ash slurries through pipes in thermal power plants can be broadly classified into two main categories namely positive displacement and centrifugal pumps. The two types of pumps differ considerably in construction as well as in operating principle compared to the conventional pumps.

The present study reports the effect of additive on the performance characteristics of centrifugal and progressive cavity screw pumps with fly ash slurries at high concentrations (above Cw < 50% by weight). Mixture of sodium carbonate and Henko detergent (5:1) at a concentration of 0.2% by weight has been used as an additive. For each type of pump, the effect of additive on the performance characteristics has been experimentally evaluated at rated speed with fly ash slurries in the concentration range of 50 to 70% by weight. The pump total head, overall efficiency and pump input power as a function of flow rate have been measured.

The results obtained from the centrifugal slurry pump performance show that at rated speed, the performance of the pump improves with the addition of drag reducing additive. In the case of progressive cavity screw pump, pump performance characteristics and behavior were completely different as compared to the centrifugal slurry pump. At rated speed, the performance of screw pump deteriorates with the addition of drag reducing soap solution.

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## Compaction of High-Ca Fly Ash-Al- and Al-Alloy-Composites: Evaluation of their Microstructure and Tribological Performance

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In this study, highly calcareous and siliceous fly ash particles were utilized for the fabrication of Al- and Al-alloy-based Metal-Matrix Composites (MMCs) by means of powder metallurgy. After compacting and sintering Al and Al/Si powders containing 10, 15, and 20wt. % ash particles, the homogenous (and with minimal amount of voids) microstructure of the produced composites was verified by means of Scanning Electron Microscopy (SEM). The composites were tested for their dry sliding wear behavior using a pin-on-disc machine against spheres of alumina. The worn surfaces of composites were then examined by using SEM and Energy Dispersive X-Ray Spectroscopy (EDS). It was shown that the addition of both types of FA enhanced the tribo-performance of Al, with the optimum metal powder replacement determined to the point of 15% wt., in the case of high-Si and 10% wt., in the case of high-Ca ash particles. Regarding alloy-matrix composites, although they generally presented worse tribological performance than pure Al/Si products, the additions of ashes up to 15% wt. resulted in only slight deterioration of the wear performance of composites.

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## Influence of Chemical Reagents on Rheological Properties of Fly Ash-Water Slurry at Varying Temperature Environment

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About 70% of total electrical energy is generated from thermal power plants in India which in turn release about 160 Mt of fly ash as solid waste annually. Transportation and disposal of such a huge amount of fly ash is a major problem faced by the power plants. Presently fly ash is transported as lean slurry in pipe lines requiring about 80 to 85% of water with high energy input.

A major impediment in high volume transportation of fly ash is its high specific gravity as compared to that of water. The objective of the present study was to evaluate the rheological characteristics of high concentration fly ash slurry with and without a chemical reagent at varying temperature environment to facilitate smooth flow of materials in the pipelines. Six different composition of fly ash slurry samples were considered for investigation. The main constituents of the slurry were fly ash, water, a cationic surfactant, and a counter-ion. Detailed rheological properties were determined using a cylindrical coaxial rotational rheometer at shear rates varying from 25s21 to 1000s21 for 40% solid concentration (by weight).

Temperature was varied from 20uC to 40uC for all the shear rates investigated. Test results showed that all the slurries exhibited shear thinning behaviour in the presence of the surfactant. The influence of cationic tenside on drag reduction of fly ash slurry was also studied. The distinctive reduction of surface tension on colloidal dispersion characteristics of the fly ash slurry was observed in the presence of the tenside. It revealed that the slurry developed in the above manner has a potential to be transported through pipelines with minimal energy consumption.

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