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

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On behalf of UK CAER and ACAA

Jim Hower, Editor-in-Chief
Tom Adams, Tom Robl

Introduction

Several methods for determining the particle size distribution (PSD) of dry powders can be found in the literature. However, there still exists a need for a more specific reference of the necessary operational parameters when analyzing supplementary cementitious materials (SCMs), such as coal combustion fly ash, gasification slag, or blast furnace slag. The optical constants that provide the most accurate and consistent PSD of fly ash, and other SCMs, are presented in this paper. The complex refractive index (RI) is an important property influencing the extinction behavior of particles. It is likely that there are no universal refractive and absorption indices for fly ash. However, these indices are required when analyzing fly ash using laser diffraction and the Mie theory. The goal of this study was to determine the appropriate complex refractive index values of SCMs, to improve the accuracy of particle-size analysis by laser diffraction.

Refractive Index Determination

The refractive index (RI) of the ash and slag samples was measured using optical microscopy (Becck Line method) and laser diffraction. As an independent method to verify the microscopy results, the laser diffraction analyzer was used to estimate the RI for a Class F fly ash using a procedure described by Malvern Instruments3. This method uses a series of dispersants with different refractive indices, while maintaining a constant mass of sample to determine the obscuration for each dispersant. The minimum obscuration percentage reflects the matching of the dispersant RI to the fly ash RI.

Results and discussion

By examining the fly ash in a series of immersion oils of different RI, the correct oil would be selected in which approximately half the particles had a RI greater than the oil and half had a lower RI than the oil. The RI of this oil represents the mean refractive index of the particles. The results from laser particle-size analysis indicated a minimum obscuration at 1.56 RI, which was consistent with the microscopy data for this sample. The RI for the fly ash and slag samples was calculated based on the weight percent of each major oxide that comprises the sample Gilard and Dubrul. Since fly ash and slag are primarily made-up of amorphous glassy material, the formula was applied to these materials and produced a refractive index trend similar to that obtained using the Becck Line method. As seen in Figure 1, a linear relationship exists between the concentration of CaO in the fly ash, or for the blast furnace slag, and the calculated refractive index. The refractive index generally increased with increasing CaO content; this trend was consistent with the microscopy data.

Summary and conclusions

Based on the foregoing, it is apparent that fly ash does not have a universal refractive index or absorption value. The results indicated that the RI of fly ash and blast furnace slag cannot be estimated if the CaO content is known. Gasifier slag did not follow the same trend, probably because of its high iron content. Based on the experiments completed in this study, fly ash with less than 10% (by weight) of CaO had an apparent absorption value of 1.0. Whereas, fly ash and blast furnace slag with greater than 10% CaO had an absorption value of 0.

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References

Zeolite synthesised from fused coal fly ash at low temperature using seawater for crystallization

Claudia Belviso, Francesco Cavalcante, Antonio Lettino, Saverio Fiore, Laboratory of Environmental and Medical Geology, IMAA–CNR, Tito Scalo (PZ), Italy.

In our study, a sample of coal fly ash from an Italian thermal power plant was used to synthesise zeolite by hydrothermal activation, after a pre-treatment fusion with NaOH. The experiments involved were performed at different temperatures of crystallization, ranging from 35°C up to 60°C, with seawater and distilled water, separately, during hydrothermal process.

As shown in Figure 1, X-ray diffraction patterns of fused fly ash, kept at 35°C, 40°C, 45°C, and 60°C, reveal that the synthesis of X-type and ZK-5-type zeolite with seawater takes place at 35°C and 45°C, respectively. The zeolite synthesis with distilled water was also done (Fig. 1b). It is evident that the amount of zeolite synthesised with seawater is higher at low temperatures, 35°C, 40°C and 60°C, respectively, than the synthesis of ZK-5-type zeolite does not take place at 45°C, when using distilled water. Minimal differences were detected in the experiments carried out at 60°C. However, only X-type zeolite is synthesised at this temperature (Fig. 1d). Besides the temperature of 35°C, X-type zeolite is synthesised (Fig. 1). The excess of NaOH used in order to form Na-P1-type zeolite with higher yields, when compared to the same process with distilled water. This difference disappears at 60°C.

Our results are not completely in accordance with the data available in literature. The synthesis of zeolite with seawater is described in a previous article, although the process involved is the hydrothermal one (without a pre-treatment fusion) used in order to form Na-P1-type zeolite with incubation temperatures above 100°C. When comparing the patterns of the products, the authors of this article report that the use of seawater neither disturbs nor accelerates the zeolite formation and the amount of zeolite synthesised with seawater is comparable that synthesised with distilled water.

In conclusion, our experiments demonstrate that a higher amount of sodium is required using seawater instead of distilled water during the hydrothermal crystallisation at temperature < 60°C. Any differences are detectable at T > 60°C with seawater or distilled water. The advantages of the process described lie in an increase in the yield of X-type zeolites, the elimination of costs for large-scale use of distilled water, and the elimination of, or drastic reduction in, the costs to attain the incubation temperature. As the X-type zeolite is formed at low temperatures with seawater, the over-flowing seawater used to cool the turbine in thermal power plants can be employed directly in this process. Most thermal power plants are situated near the coast, and a lot of seawater containing waste heat is eliminated. The use of seawater, as an artificial zeolite synthesis, could reduce the heating energy and the cost of water. The seawater used to cool the turbines of electric power plants can be recycled for the X-type zeolite synthesis without employing any other type of energy or with a reduced energy input, to further increase an incubation temperature in the zeolite production process. Zeolite X synthesized, according with its particular three-dimensional ordered structure and strictly connected with the ability to exchange cations and the large surface area, may be used as industrial products in concrete and cement manufacturing. They may also be useful for reducing both the amount and the mobility of metals in a number of environmental applications.

References

Coal combustion has been reported to be the largest single source of anthropogenic mercury emissions. In 2004, 38% of these emissions in Europe originated from coal combustion. As a consequence, legislative bodies have focused their attention on reducing mercury emissions from coal fired power plants1-3. During the last few years different options for mercury reduction from coal combustion have been evaluated. To date, a cost-effective technology has not yet been developed. Some of these technologies are based on the retention of mercury in sorbents. Activated carbons are considered to be effective sorbents for mercury control in flue gas from coal combustion4-6. However, more economical sorbents, such as fly ashes, also need to be studied. Recent research has shown that certain fly ash materials are able to capture different amounts of Hg, the quantity varying from one fly ash to another, depending on the fly ash characteristics1-2.

In this work, the mercury retention capacity of different fly ashes was compared with retention by commercial activated carbons in different experimental conditions. It reviews the influence of different variables on mercury capture, including the composition and nature of the sorbents, the composition of the flue gas, and the mercury species in gas phase. The sorption experiments were carried out in a laboratory scale device using a simulated flue gas and nitrogen atmosphere.

A comparison between the results, obtained from the fly ash and activated carbon samples, demonstrates that the amount of carbon is a good indicator of the capacity to retain mercury. The retention of Hg₂⁺ is greatly influenced by the gas atmosphere. Although the efficiency of the mercury retention was higher in activated carbons than in fly ashes, some activated carbon showed a lower retention capacity for Hg²⁺ than some fly ashes in the simulated flue gas. This suggests that surface area is not the main factor affecting retention, even though it may control the kinetics of the process. The retention of HgCl₂ in the commercial activated carbons, which may involve physical adsorption, is higher than in most fly ashes.

Acknowledgements
The results of this work were obtained as part of the projects: PPQ2001-3599-C02-02 and CTM2004-0452-C02-02/TECNO

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In conclusion, our experiments demonstrate that a higher amount of zeolite can be obtained using seawater instead of distilled water during the hydrothermal crystallisation at temperatures ≤ 60°C. Any differences are detectable at T ≥ 60°C with sea or distilled water. The advantages of the process described lie in an increase in the yield of X-type zeolites, the elimination of costs for large-scale use of distilled water, and the elimination of, or drastic reduction in, the costs to attain the incubation temperature. As the X-type zeolite is formed at low temperatures with seawater, the outflowing seawater used to cool the turbine in thermal power plants can be employed directly in this process. Most thermal power plants are situated near the coast and a lot of seawater is available in that area. Although the efficiency of the mercury retention was not the main factor affecting retention, even though it may control the kinetics of the process. The retention performance of HgCl₂, the commercial activated carbon, which may involve physical adsorption, is higher than in most fly ashes.

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Coal-fired power-station-ash products and EU regulation
Lindon K. A. Sears, UK Quality Ash Association, Wolaverhamp ton, West Midlands, United Kingdom.

The UK has a long history of the use of coal-fired power-station-ash products in a range of applications in construction. These range from use in concrete as a cementitious material through to use as a fill material in embankments. While there have been no environmental problems associated with these uses, environmental regulations emanating from the European Union (EU) are increasingly impacting the use of these materials. Unfortunately, it is not a single set of regulations that are being applied, but there separate and apparently disconnected initiatives: Registration, Evaluation, and Authorisation of Chemicals (REACH); Essential Requirement 3 (ER3); and the Waste Framework Directive (WFD).

Coal-fired-ash products, such as fly ash (FA) and furnace bottom ash (FBA), are treated by the Environment Agency (EA) for England and Wales as waste materials falling under the Waste Framework Directive (WFD). Being classified as a waste, theoretically, leads to a series of exemptions and licences being required before use of these materials in construction applications involving the contractor in expense and time. In practice, the EA has taken a reasonably pragmatic approach in the majority of cases, but the WFD has clearly had a negative impact on ash sales. In order to alleviate this bureaucracy, the principle of defining ‘end of waste’ criteria was created using a document called a ‘Quality Protocol’ (QP) for FA and FBA. After many years of work, the document is due to be published in 2010.

While the requirements of the QP protect the environment from any perceived threat from FA and FBA, a separate regulation, REACH, was imposed against industry for all chemical products placed on the market. As the QP defined when FA and FBA cease to be wastes, they are thereby other products which have to be registered under REACH. If the QP and REACH were not sufficient protection to the environment, ER3 is being implemented through product standards, which places limit values on potentially polluting toxic compounds. Of course, the testing standards being applied for these three initiatives are potentially all very different.

The result of this tri-reegulation approach within the EU is duplication and excessive bureaucracy on products that have a proven track record. While the UK government’s and EU’s stated aim is to encourage recycling, these various regulations will have the opposite effect.

The full-text version of this paper will outline the requirements of these regulations and detail some of the problems associated with compliance, the production, and supply of power station ash products in the UK.

Erosive wear in pipelines at pneumatic conveying of fine silicon-containing materials
Vladimír V. Putilova, Moscow Power Engineering Institute (MPEI), Informational and Analytical Center “Ecology in Power Engineering”, Moscow, Russia; Vijay K. Agarwal Indian Institute of Technology (IITD), Hauz Khas, New Delhi, India; Irina V. Putilova, Moscow Power Engineering Institute (MPEI), Department of Boiler Plants and Ecology of Power Engineering, Moscow, Russia.

Erosive wear is a major operational problem in conveying of hard abrasive materials in pneumatic conveying systems. Silicon-containing materials, like silica sand or fly ash, have very high hardness value and lead to erosive wear, due to high velocity impact of such particles on the target surface. Erosion in pipelines is observed owing to interaction of particles of the transported material with a wall of a pipe. Consequently, microscopic metal chips of the pipeline are cut off. This interaction is carried out by the turbulent two-phase flow with a large Reynolds number and therefore, transported particles attack a wall of the pipeline at angles which cannot be defined theoretically and described mathematically.

In comparison with other elements of pneumatic conveying installation, the increased erosion is observed in curvilinear sections of pipelines, namely in those places where the axis of a dust flow is directed angularly to a surface of pipelines. These elements are: locking and regulating armature, bends of pipelines, T-joints, transitions, and flow switches. Rectilinear sections of pipelines are subject to erosion, essentially less than curvilinear ones. Estimation of erosion for curvilinear pipelines sections of pneumatic transport installations is much more complex than for rectilinear pipelines.

For more than 10 years, employees of the Informational and Analytical Center “Ecology in Power Engineering” (IACEE MPEI) and department Boiler Plants and Ecology of Power Engineering of the Moscow Power Engineering Institute (Technical University) (MPEI(TU)), have been carrying out research works on erosion in pipelines at pneumatic transportation of fine, bulk silicon-containing materials. As a result of completing the research, a model of estimating erosive wear in rectilinear and curvilinear sections of pneumatic conveying pipelines has been developed. The model takes into consideration the properties of the material being conveyed and the major operating variables.

To validate the model developed in the MPEI for estimating erosive wear in the pneumatic pipelines, employees of the MPEI and IITD completed the first set of the joint experimental investigations on a pilot plant of the IITD in 2009. Investigations on this project are to be carried on in 2010-2011, according to the agreement on the Indo-Russian scientific and technical collaboration. The project is financed by the Russian Foundation for Basic Research (RFBR) and Department of Science and Technology of the Government of India. The pneumotransport installation has been modified for carrying on corresponding scientific investigations.

An investigation of the behavior of raw calcareous fly ash in mortar mixtures
Ioanna Papayianni, Eleftherios K. Anastasiou, Aristotle University of Thessaloniki, Department of Civil Engineering, Laboratory of Building Materials, Thessaloniki, Greece.

There are only a few standards covering the use of calcareous fly ash in construction applications and this is partially due to the particularity of the material, which contains three reactive constituents: lime (CaO), silica (SiO2), and sulfates (SO3). The aim of this experimental research was to find how these three, more reactive constituents of calcareous fly ash, influence the behavior of fly ash or cement-fly ash mortar mixtures. Another aim was to identify which one of them is of greater significance for strength and volume stability. An effort was made to explain their behavior by subjecting these fly ashes and mortars to different tests.

The two calcareous fly ashes tested (named Ptol I and Ptol II) were selected for their differences in reactive silica, available lime content, and sulfates. The first sample (Ptol I) was of high lime and sulfate value, while the second had less than 4% SO3.

One cement type, CEM I 42.5 mortar, was used as control, two cement-fly ash mortars were prepared in order to determine Ptol I and II pozzolanicity index with cement, and two lime-fly ash mortars were prepared in order to determine Ptol I and II pozzolanicity index with lime. Eight more mortar mixtures were also prepared: two with Ptol I and Ptol II as the only binder and two with cement-fly ash + 50/50 combinations. These four mortars were repeated using superplasticizers to adjust consistency.

Results from the laboratory tests carried out on the ashes Ptol I and II and the mortars produced are shown in the following Table.

The methodology prescribed in EN 196–2 were used for reactive SO2, LOI, and SO3 determination, while the available lime content was determined according to EN 451–1. The free Ca(OH)2 (non-hydrated) was determined by subtracting the amount of CaOH2 from the available lime. The amount of CaOH2 was determined by the DTA-TG method. Alkalis and chlorides were measured according to EN 196–21 and the mineralogical phases of dry fly ash, as recognized in x-ray diffraction diagrams. R,5% fineness measured by scientific and technical collaboration. The project is financed by the Russian Foundation for Basic Research (RFBR) and Department of Science and Technology of the Government of India. The pneumotransport installation has been modified for carrying on corresponding scientific investigations.
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There are only a few standards covering the use of calcareous fly ash in construction applications and this is partially due to the particularity of the material, which contains three reactive constituents: lime (CaO), silica (SiO2), and sulfates (SO3). The aim of this experimental research was to find how these three, more reactive constituents of calcareous fly ash, influence the behavior of fly ash or cement-fly ash mortar mixtures. Another aim was to identify which one of them is of greater significance for strength and volume stability. An effort was made to explain their behavior by subjecting these fly ashes and mortars to different tests.

The two calcareous fly ashes tested (named Ptol I and Ptol II) were selected for their differences in reactive silica, available lime content, and sulfates. The first sample (Ptol I) was of high lime and sulfate value, while the second had less than 4% SO3.

One cement type, CEM I 42.5 N, was used as control, two cement-fly ash mortars were prepared in order to determine Ptol I and II pozzolanicity index with cement, and two fly-ash mortars were prepared in order to determine Ptol I and II pozzolanicity index with lime. Eight more mortar mixtures were also prepared: two with Ptol I and Ptol II as the only binder and two with cement/lime-fly ash = 50/50 combinations. These four mixtures were repeated using superplasticizers to adjust consistency.

Results from the laboratory tests carried out on the ashes Ptol I and II and the mortars produced are shown in the following Table. The methodologies prescribed in EN 196-2 were used for reactivity SO3, LOI, and SO3 determination, while the available lime content was determined according to EN 451-1. The free CaO (non-hydrated) was determined by subtracting the amount of Ca(OH)2 from the available lime. The amount of Ca(OH)2 was determined by the DTA-TG method. Alkalis and chlorides were measured according to EN 196-21 and the microscopic phases of fly ash fly ash, as recognized using a scanning electron microscopy (SEM), are shown in diffractograms. R45_m fineness was measured by the Russian Foundation for Basic Research (RFBR) and Department of Science and Technology of the Government of India. The pneumoconveying installation has been modified for carrying on corresponding scientific investigations.
Chemistry of coal and coal combustion products from Kentucky power plants: Results from the 2007 sampling with emphasis on selenium

James C. Hower, Thomas L. Robl, Gerald A. Thomas, Shelley D. Hopp, Margaret Grider, University of Kentucky, Center for Applied Energy Research, Lexington, Kentucky.

Kentucky produced over 8 Mt of coal combustion products (CCPs) in 2006, with 30% of the CCPs being utilized. This represents a significant increase from 1996 and 2001, when 10% and 20%, respectively, of CCPs were utilized. Much of this material is utilized in combination with fly ash and mortars.

Regarding fly ash mortars, the consistency of all mortars was measured using a box table expander and was, at least, greater than 4.2 cm and 4.8 cm. The same consistency was achieved for low-flying ash, Proef 1 and Proef 2, with and without addition of superplasticizer (SPL). Furthermore, the early shrinkage deformations of the mortars without SPLs were monitored while being cured at 20 °C and ±6% relative humidity, in order to test higher water/cementitious ratios influence the shrinkage. Soundness values of the cement-fly ash combinations do not present values above limits for both fly ashes.

The soundness index for Proef 1 and Proef 2 is 93% and 81% of the control cement strength, respectively. The 7-d strength is also higher for the Proef 1 and reaches 86% of the corresponding cement strength. However, the rate of strength development from 7-d to 28-d is higher in the case of Ptol II sample.

In this paper, and to the best of our knowledge, for the first time a carbonation-accelerated process has been carried out in fly ash based geopolymer S/S solids, with the aim of studying its influence in mechanical and leaching properties. A general view of the carbonation system is shown in Figure 1.

EAF dust is generally classified as hazardous waste by many regulations because of its high level of heavy metals, such as Pb, Cd, Cr, or Zn. Stabilization/solidification (S/S) technique has been used worldwide to treat this residue. Although EAF dust is a waste product difficult to stabilize, the use of different S/S systems may be found in the literature. Geopolymer technology has recently received attention in waste stabilization/solidification (S/S) systems of heavy-metal-containing wastes. They showed good chemical and physical properties, such as structural integrity, low permeability, high compressive strength, and durability.

The effect of the curing in a carbonated ambient of the solids obtained after the stabilization/solidification (S/S) of metallurgical waste, using geopolymerization technology, is described in this paper. It has been reported that carbonation may directly alter the chemical and physical properties of solidified waste forms.

In this paper, and to the best of our knowledge, for the first time a carbonation-accelerated process has been carried out in fly ash based geopolymer S/S solids, with the aim of studying its influence in mechanical and leaching properties. A general view of the carbonation system is shown in Figure 1.

Figure 1. General view of carbonation test

Low-calcium fly ash (ASTM class F) from the combustion of high-quality pulverized coal was used as the main siliciclanium source. Fly furnace dust (FFD) as a lime and silicon within the ash collection systems. In some cases, there is an increase in Si concentration towards the cooler ESP rows. In one power plant, the relatively high Si concentrations in the first ESP row, observed in samples collected in 2001 and 2002, were not observed in the 2007 samples. In the latter case, the reconfiguration of the ash-collection system might have played a role in the exit element distribution.

Full paper available at: www.coalcgp-journal.org
James C. Hower, Thomas L. Robl, Gerald A. Thomas, Shelley D. Hopps, Margaret Grider, plants: Results from the 2007 sampling with emphasis on selenium

Regarding fly ash mortars, the consistency of all mortars was measured using a table expansion and was stable, measuring from 14.2 cm to 14.8 cm. The same consistency was achieved for the two fly ashes, Ptol I and Ptol II, with and without addition of superplasticizer (SPL). Furthermore, the early shrinkage deformations of the mortar mixtures with and without SPL were monitored while being cured at 20°C and 65% relative humidity, in order to test if higher water/cementitious ratios influence the shrinkage. Soundness values of the cement-fly ash combinations do not present values above limits for both fly ashes.

The soundness index for Ptol I and Ptol II is 93% and 81% of the control cement strength, respectively. The 7-d strength is also higher for the Ptol I and Ptol II samples and represents a significant increase from 1996 and 2001, when 70% and 68% of the control cement strength was achieved for the two fly ashes, Ptol I and Ptol II, respectively. Earlier shrinkage was also improved. Shrinkage deformations up to 28-days of age are also higher for the Ptol II mortar mixtures.

When 50% of cement mass is replaced by these fly ashes, the strength values are 42.0 MPa to 48.7 MPa. The prediction of the behavior of calcareous fly ashes, based on their chemical composition, does not represent their reactivity in mortar mixtures. It seems that it is more realistic and effective to use the actual combination of cement-fly ash admixtures for a predetermined strength level at a certain age, in order to test the suitability of calcareous fly ashes.

Chemistry of coal and coal combustion products from Kentucky power plants: Results from the 2007 sampling with emphasis on selenium

James C. Hower, Thomas L. Robl, Gerald A. Thomas, Shelley D. Hopps, Margaret Grider, University of Kentucky, Center for Applied Energy Research, Lexington, Kentucky.

Kentucky produced over 8 M t of coal combustion products (CCPs) in 2006, with 30% of the CCPs being utilized. This represents a significant increase from 1996 and 2001, when 10% and 20%, respectively, of CCPs were utilized. Much of this trend is related to the increased utilization of flue gas desulfurization (FGD) gypsum. Therefore, considering the increased production of FGD gypsum, coincident with the commissioning of new FGD units and the amelioration of the (currently) weak market for new construction, the percentage of utilization may decrease by the time of the next planned survey (2011).

The concentration of volatile trace elements in the feed coal and in the pulverized coal, while associated with pyritic sulfur, are somewhat independent of the pyritic sulfur content owing to proportional variation in the trace element content of coal minerals. Consequently, high-pyrite-high-S coal does not necessarily produce the highest As, Se, and Hg (among other elements) fly ashes. Among the power plants in Kentucky, plants with intermediate sulfur contents have some of the highest concentrations of volatile trace elements in their fly ashes.

In the four and second row ESP fly ashes, there is a general increase in Fe2O3, CaO, and SO3, and an accompanying decrease in SiO2 and Al2O3, with an increase in the S content of the feed coal. In general, volatile trace elements, such as Zn and As in fly ash, increase in concentration from the first to the last row of the pollution control system, owing to the decrease in flue gas temperature and decrease in particle size (and increase in surface area of the Al2O3 particle) in that direction. Mercury is dependent upon the carbon content and the surface area of the carbon, in addition to the flue gas temperature. Mercury capture by fly ash increases with (1) an increase in carbon content, (2) an increase in the surface area of the carbon, and (3) a decrease in the flue gas temperature. Selenium is more problematical, depending on its transformation within the ash collection systems. In some cases, there is an increase in Se concentration towards the cooler ESP rows. In one power plant, the relatively high Se concentrations in the first ESP row, observed in samples collected in 2001 and 2002, were not observed in the 2007 samples. In the latter case, the reconfiguration of the ash-collection system might have played a role in the trace element distribution.

EAF dust is generally classified as hazardous waste by many regulations because of its high level of heavy metals, such as Pb, Cd, Cr, or Zn. Stabilization/solidification (S/S) technique has been used worldwide to treat this residue. Although EAF dust is a waste product difficult to stabilize, the use of different S/S systems may be found in the literature. Geopolymer technology has recently received attention in waste stabilization/solidification (S/S) systems of heavy-metal-containing wastes. They showed good chemical and physical properties, such as structural integrity, low permeability, high compressive strength, and durability. The effect of the curing in a carbonated ambient of the solids obtained after the stabilization/solidification (S/S) of metallurgical waste, using geopolymerization technology, is described in this paper. It has been reported that carbonation may directly alter the chemical and physical properties of solidified waste forms.

In this paper, and to the best of our knowledge, for the first time a carbonation-accelerated process has been carried out in fly ash based geopolymer S/S solids, with the aim of studying its influence in mechanical and leaching properties. A general view of the carbonation system is shown in Figure 1.

Figure 1 General view of carbonation test

Low-calcium fly ash (ASTM class F) from the combustion of high-quality pulverized coal was used as the main siliciculminate source. Blown furnace slag (BFS), as a lime and silicon source, and kaolinite as a secondary siliciculminate source were also used. Potassium silicate was used as geopolymer liquid. Ordinary Portland cement (OPC, type II) was used in order to compare geopolymer stabilization/solidification (S/S) process with a conventional S/S process using OPC, lime, and fly ash.

Compressive strength test and leaching tests (UNE-EN 12457-4, USEPA TCLP, NEN 7341, GANC-General Acid Neutralization Capacity–and NEN 7340) were carried out to assess the efficacy of the S/S process.

Compressive strength values, far better than those achieved by hydraulic S/S methods, were easily obtained by geopolymer solids at 28 days. Carbonation produced a great increment of compressive strength in samples containing a higher K2O proportion.

UNE-EN12457-4 Zn leachate concentrations decreased in samples cured in carbonated atmosphere, but leachability increased slightly with the carbonation time in all the samples. In general, lead concentration also increased with the carbonation time. In spite of this, Pb showed a high degree of immobilization in geopolymer matrices. Carbonation reduced pH in OPC samples and consequently their TCLP Zn, Pb, and Cd leachate concentrations decreased. In general, carbonation also improved Zn, Pb, and Cd leachabilities for samples prepared with geopolymer agents. Carbonation time produced a metal concentration decrease in TCLP leachates.

In general, NEN 7345 tank leaching test results evidenced the leaching benefit of geopolymeric techniques in non-carbonated ambient, especially for Pb and Cr. Zn concentrations were low, using both conventional and geopolymeric methods.

Cadmium concentrations were under the detection limits in all samples. Carbonation caused a clear reduction of the NEN 7345 Cr and Pb leachate concentrations for geopolymer samples with time, whereas the effect in OPC samples was the opposite. Carbonation did not significantly affect the acid neutralization capacity (GANC) of the studied geopolymer S/S solids and therefore, important changes in the Zn, Pb, Cr, and Cd leachabilities, with time, are not expected.

Generally, the leachate pH reduction in all the leaching tests is important regarding the stability of the S/S solids with time. The better response of the geopolymer S/S solids regarding this property implies a clear advantage for geopolymer S/S solids over OPC S/S solids.

Full paper available at: www.coalgp-journal.org
Variations in fly ash composition with sampling location: Case study from a Portuguese power plant

B. Valentim, A. Guedes, D. Flores. Centro e Departamento de Geologia Faculdade de Ciências da Universidade do Porto, Porto, Portugal, C.R. Ward, School of Biological, Earth and Environmental Sciences, University of New South Wales, Australia. J.C. Hower, University of Kentucky, Center for Applied Energy Research, Lexington, Kentucky, USA.

Fly ash (FA) is a heterogeneous and complex material, resulting from coal combustion in thermoelectric power plants (TPPs). Different types of coal, worldwide, produce FAs with different compositions. However, the location of the FA sampling points, inside the TPP, is also important with respect to the composition of the FA produced at each location. A case study of FA from a Portuguese 650-MW TPP, equipped with low-NOx burners using several coal and FA characterization techniques (particle size analysis, proximate and ultimate analyses, XRF, SEM/EDS, optical microscopy, XRD, and AAS), has shown that the chemical classification, mineralogy, phase-mineral classification, and trace element characteristics (Cr, Cu, Mn, Ni, Pb, and Zn) of the ash vary significantly with sampling location. The feed for the study was a 50:50 blend of Sialic and Calsialic coals (El Cerrejon and Kangra). Although the resulting fly ash plots between the HTAs of the individual coals blended to constitute the feed, none of the FAs have the same chemical classification. Variations in alkaline and Fe oxides result in variations in the chemical classification of the individual ash samples (Figure 1). The relative enrichment (RE value) of the trace elements studied (except Mn) also shows variation with the sampling location (Figure 2) and with the fly ashes from the upstream end (Economizer) to the downstream end (ESP-h 42) of the ash flow path, being progressively enriched in Cr, Cu, Ni, Pb, and Zn. This has implications for improved understanding of the combustion system, as well as in collecting ash products from TPPs for particular mark applications.

Acknowledgements

The authors thank the Fundação para a Ciência e a Tecnologia (Portugal) and FEDER (UE) for financing the Project, Contract POCI/CTA/34997/2002.

Mechanical performance of pavement geomaterials stabilized with fly ash in field applications

Lin Li, Department of Civil and Environmental Engineering, Jackson State University, Jackson, Mississippi, USA. Tuncan B. Edil, Craig H. Benson, Recycled Materials Resource Center, Department of Civil and Environmental Engineering, University of Wisconsin-Madison, Madison, Wisconsin, USA.

Fly ash stabilized with fly ash in field applications

The full-text version of this paper describes an evaluation of the mechanical performance of fly ash stabilized materials, including soft clay soil, asphaltic recycled pavement material (RPM), and road-surface gravel (RSG) at six sites in Wisconsin and Minnesota (Table 1). The CBR and off-specification fly ashes were used in the stabilization to create concrete platforms or to stabilize base courses for construction of flexible and rigid pavements. For California bearing ratio (CBR), resilient modulus (M r), and unconfined compression (q u) tests, were conducted on the subgrade soil, RPM, and RSG alone. They were also conducted on mixtures prepared in the field and the laboratory, to evaluate improvements in bearing resistance and stiffness. Fly ash stabilization improved the stiffness and strength of the materials significantly. After 7 d of curing, CBR of the stabilized materials (10 to 150) was two to ten times the CBR of the materials alone (1 to 50). The M r of the stabilized materials ranged between 20-200 MPa after 14 d of curing, whereas the M r of the materials alone was 10-120 MPa. The q u of the unstabilized subgrade is in average of 120 kPa, and the field-mix fly ash stabilized materials have q u between 254 kPa and 368 kPa (mean ± 311 kPa). The FASM had significantly higher CBR, M r, and q u than the pavement materials, which suggests that the FASM should be beneficial in terms of increasing pavement capacity and service life. However, the CBR, M r, and q u of most FASM mixed in the field, were lower than those for FASM mixed in the laboratory (30%-66% lower for CBR, 25%-52% lower for M r, 43% lower for q u, on average). Similar biases between mixtures prepared in the laboratory and field have been observed by others, and need to be considered when pavement design is based on data obtained by testing mixtures blended in the laboratory.

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Table 1. Pavement Structure and Materials at the six sites

<table>
<thead>
<tr>
<th>Location</th>
<th>Subgrade soil</th>
<th>RPM</th>
<th>RSG</th>
<th>M r</th>
<th>q u</th>
<th>CBR</th>
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<tr>
<td>City street</td>
<td>Staged materials (10 to 150)</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>City street</td>
<td>RPM</td>
<td>FASM</td>
<td>SRSG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>City street</td>
<td>Base material</td>
<td>SF</td>
<td>ES</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>City street</td>
<td>Fly ash</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>City street</td>
<td>Off-specification</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>City street</td>
<td>Pavement material</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>City street</td>
<td>Pavement material</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>City street</td>
<td>Pavement material</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>City street</td>
<td>Pavement material</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>City street</td>
<td>Pavement material</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Box plot of mechanical properties of pavement materials and fly ash stabilized materials (laboratory-mix and field-mix): (a) CBR after 7 d of curing; (b) M r after 14 d of curing.
Fly ash (FA) is a heterogeneous and complex material, resulting from coal combustion and gasification processes in thermoelectric power plants (TPPs). Different types of coal worldwide produce FAs with different compositions. However, the location of the FA sampling points, inside the TPP, can also greatly affect the properties of the FA produced at each location. A case study of FA from a Portuguese 630 MW TPP equipped with low-NOx burners using several coal and FA characterization techniques (particle size analysis, proximate and ultimate analyses, XRF, SEM/EDS/EDX, optical microscopy, XRD, and AES), has shown that the chemical classification, mineralogy, phase-mineral classification, and trace element characteristics (Co, Cu, Mn, Ni, Pb, and Zn) of the ash vary significantly with sampling location. Fly ash for the study was a 50:50 blend of Safic and Calsialic coals (El Cerrejón and Kangra). Although the resulting fly ashes plot between the HTAs of the individual coals blended to constitute the feed, none of the FAs have the same chemical classification. Variations in alkaline and Fe oxides result in variations in the chemical classification of the individual ash samples (Figure 1). The relative enrichment (RE value) of the trace elements studied (except Mn) also shows variation with the sampling location (Figure 2) and with the fly ashes from the upstream end (Economizer) to the downstream end (ESP-h42) of the ash flow path, being progressively enriched in Co, Cu, Pb, Ni, and Zn. This has implications for improved understanding of the combustion system, as well as in collecting ash products from TPPs for particular market applications.

### Acknowledgements
The authors thank the Fundação para a Ciência e a Tecnologia (Portugal) and FEDER (UE) for financing the Project, Contract POCTI/CTA/38997/01.

### Table 1. Pavement Structure and Materials at the six sites

<table>
<thead>
<tr>
<th>Sites</th>
<th>Scenic Edge</th>
<th>STH 60</th>
<th>STH 32</th>
<th>USH 12</th>
<th>Waseca</th>
<th>Chisago</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>City street in Case Plaza, Wisconsin</td>
<td>State highway, Wisconsin</td>
<td>State highway, Wisconsin</td>
<td>US Highway, Wisconsin</td>
<td>City street in Waseca, Minnesota</td>
<td>Highway CR 55, Minnesota</td>
</tr>
<tr>
<td>Project length</td>
<td>790 m</td>
<td>385 m</td>
<td>370 m</td>
<td>1200 m</td>
<td>500 m</td>
<td>3500 m</td>
</tr>
<tr>
<td>Surface material</td>
<td>100 mm-FHM</td>
<td>125 mm-FHM</td>
<td>220 mm-PCC</td>
<td>200 mm-PCC</td>
<td>75 mm-FHM</td>
<td>89 mm-FHM</td>
</tr>
<tr>
<td>Base material</td>
<td>157 mm-CA</td>
<td>225 mm-CA</td>
<td>200 mm-CA</td>
<td>150 mm-CA</td>
<td>150 mm-SPRM</td>
<td>254 mm-SRSG</td>
</tr>
<tr>
<td>Subbase material</td>
<td>300 mm-FASM</td>
<td>300 mm FASM</td>
<td>300 mm-FAAM</td>
<td>300 mm-FAAM</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Note: STH = state trunk highway, HMA = hot mix asphalt, PCC = Portland cement concrete, CA = crushed aggregate, FASM = fly ash stabilized material, RPM = recycled pavement material, RSG = road-surface gravel, SRPS = stabilized recycled pavement material, SRSG = stabilized road-surface gravel, N/A = not applicable. *Class C fly ash in dry weight, mixing of Class C and off specification fly ash in 1:1 mixing ratio.

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#### Fly ash stabilization in field applications

Fly ash stabilization is used in flexible and rigid pavements. California bearing ratio (CBR), resilient modulus (M_r), and unconfined compression (q_u) tests, were conducted on the subgrade soil, RPM, and RSG alone. They were also conducted on mixtures prepared in the field and the laboratory, to evaluate improvements in bearing resistance and stiffness. Fly ash stabilization improved the stiffness and strength of the materials significantly. After 7 days of curing, CBR of the stabilized materials (10–150) was two to ten times the CBR of the materials alone (1 to 50). The M_r of the stabilized materials ranged between 20-200 MPa after 14 days of curing, whereas the M_r of the materials alone was 10–120 MPa. The q_u of the unstabilized subgrade is in average of 121 kPa, and the field-mix fly ash stabilized materials have q_u between 254 kPa and 368 kPa (mean = 311 kPa).

The FASM had significantly higher CBR, M_r, and q_u than the pavement materials, which suggests that the FASM should be beneficial in terms of increasing pavement capacity and service life. However, the CBR, M_r, and q_u of most FASM mixed in the field, were lower than those for FASM mixed in the laboratory (30%-66% lower for CBR, 25%-52% lower for M_r, 43% lower for q_u, in average). Similar biases between mixtures prepared in the laboratory and field have been observed by others, and need to be considered when pavement design is based on data obtained by testing mixtures blended in the laboratory.

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### Table 1. Enrichment factors (RE) of the trace elements.

<table>
<thead>
<tr>
<th>Trace element</th>
<th>Economizer</th>
<th>Air-heater</th>
<th>FASM-h42</th>
<th>ESP-h42</th>
<th>FAS</th>
<th>M</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>2.5</td>
<td>1.7</td>
<td>4.2</td>
<td>2.3</td>
<td>1.0</td>
<td>1</td>
<td>1</td>
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<tr>
<td>Mn</td>
<td>6.8</td>
<td>5.7</td>
<td>9.3</td>
<td>6.2</td>
<td>1.0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ni</td>
<td>4.2</td>
<td>4.0</td>
<td>6.1</td>
<td>4.5</td>
<td>1.0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Pb</td>
<td>3.1</td>
<td>2.9</td>
<td>4.8</td>
<td>3.5</td>
<td>1.0</td>
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<tr>
<td>Zn</td>
<td>2.9</td>
<td>2.7</td>
<td>4.1</td>
<td>3.2</td>
<td>1.0</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Note: Economizer: c) Economizer; d) Air-heater; x) ESP-h42; f) ESP-h42, FA glass; g) Economizer (h) Air-heater; j) ESP-h42; s) Economizer (k) Air-heater; j) ESP-h42; s) Economizer (l) Air-heater; j) ESP-h42; (m) Economizer; i) ESP-h12; J) ESP-h42. S: Safic; FS: Ferrisialic; CS: Calsialic; (l) Right-phase mineral classification of fly ashes from four sampling locations inside a power plant: a) Economizer; b) Air-heater; c) ESP-h12; d) ESP-h42; P: Pozzolanic; I: Inert; M: Mixed; A: Active.
A series of laboratory-based leaching tests has been developed to evaluate the chemical interaction between ash, water, and different mine-site rock materials, as a basis for assessing the potential environmental impact of using coal ash as backfill in coal mines. Two different test protocols were used:

- Two-stage serial batch testing program, in which leachate from representative ash samples was allowed to interact separately with relevant rock materials under laboratory conditions.
- Single-stage mixed batch testing program, in which 50:50 mixtures of the same ashes and rock samples were extracted with water following a similar procedure to leaching tests used for the individual ash and rock samples.

The concentrations of major and trace elements released in both studies were compared to the concentrations expected from the leaching characteristics of the individual ash and rock samples, when tested alone. In both the serial tests and the mixed-batch tests, these showed markedly lower concentrations of several key elements in solution (e.g. Mo, As, Se) after interaction of the ash leachate with the rock samples. The results indicate that some elements released from the ash in a mine backfill may be attenuated to a significant extent when the leachate comes into contact with other rock materials. The extent of attenuation was greater for rocks with high proportions of clay minerals (e.g. shales) or Fe oxy-hydroxides (e.g. iron-stained sandstones). Rocks with lower clay or Fe oxy-hydroxide contents, such as white quartz sandstones, apparently have lesser attenuating effects.

The attenuation properties appear to be related to the nature of the rock in question. Test programs of this type may provide a useful basis for assessing the potential impacts of placing different ashes in close association with relevant rock areas in mine backfill and similar applications. Although testing for any individual site should also consider the design of the proposed backfill, the regional hydrogeology and the results of other site investigations, collection, and evaluation of data from one or both protocols, may be of value in more fully understanding and predicting the environmental impact of ash-based mine backfill programs.

Germanium is present in the fly ash of the 335-MW ELCOGAS S.A., 13500 Puertollano, Ciudad Real, Spain. The valorization of coal gasification fly ash was studied by precipitating trace amounts of Ge from the leachate with cetyl-trimethyl-ammonium bromide (CTAB) and catechol (CAT). The global reaction can be depicted as follows:

\[
[\text{CTA}^+\text{Ge(CAT)}^-] \leftrightarrow [\text{Ge(CAT)}^-] + \text{CAT} 
\]

\[
T=340^\circ\text{C} \quad (4) 
\]

\[
2 \text{Ge(O}_2\text{Ge}) \rightarrow 2 \text{GeO}_2 + \text{Ge} 
\]

\[
T=600^\circ\text{C} \quad (6) 
\]

The precipitation of Ge as an organic complex with CAT and CTAB was found to be selective towards Ge and this element can be effectively separated from As, Mo, Se, V, Zn, or Zn, as can be seen in Table 1.

<table>
<thead>
<tr>
<th>Leachate</th>
<th>Test No. 1</th>
<th>Test No. 8</th>
<th>Test No. 9</th>
<th>Test No. 10</th>
<th>Test No. 11</th>
<th>Test No. 17</th>
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<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
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<tr>
<td>As</td>
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<td>13.3</td>
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</tr>
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<td>13.1</td>
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<tr>
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<td>0.9</td>
<td>0.08</td>
<td>0.89</td>
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<tr>
<td>Zn</td>
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<td>0.04</td>
<td>91</td>
<td>0.28</td>
<td>86</td>
<td>0.24</td>
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</tbody>
</table>

The precipitation of Ge in the water leachate is virtually the same as Ge. The precipitation yields were high in all tests and therefore, it could become an important interference in the precipitation. The order of interference of other metals is as follows: No > Zn > Mo > V > As.

Germanium precipitation is also possible from catechol leachates by adding only CTAB (38%). The main interference in this case is also Ni.

Total organic carbon was measured and results allowed estimation of the CAT and CTAB precipitated with Ge and interferences.

Thermo-gravimetric analyses performed to the Ge-complex solid revealed the following evolution:

1. From room temperature to 100°C the loss of water occurred.
2. In the range 180°C - 290°C, a 24.5% of mass was reduced.
3. The reduced mass in the second step was 19.0%.
4. The following step began at 340°C and the mass loss was 24.4%.
5. The last step began at around 500°C.
6. At constant weight, the roasted precipitate had 16.9% of the initial precipitate mass.

Taking into account this following mechanism for the decomposition of the Ge-complex is proposed:

\[
[\text{CTA}^+\text{Ge(CAT)}^-] \rightarrow [\text{Ge(CAT)}^-] + 2\text{CTA} 
\]

\[
T=180^\circ\text{C} \quad (2) 
\]

\[
[\text{Ge(CAT)}^-] \rightarrow [\text{Ge(CAT)}] + 2\text{CAT} 
\]

\[
T=300^\circ\text{C} \quad (3) 
\]

\[
[\text{Ge(CAT)}] + \text{Ge} \rightarrow \text{CAT} + \text{Ge}_2 \text{O}_3 
\]

\[
T=340^\circ\text{C} \quad (4) 
\]
Testing of interactions between coal ash leachates and rock materials for mine backfill evaluations

Colin R. Ward, Zhongheng Li, Leanne Stephenson, School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney 2052, Australia. Colin R. Ward, David French, Ken Riley, CSIRO Energy Technology, PMB 7 Menai 2234, Australia.

A series of laboratory-based leaching tests has been developed to evaluate the chemical interaction between ash, water, and different mine-site rock materials, as a basis for assessing the potential environmental impact of using coal ash as backfill in coal mines.

Two different test protocols were used:

- Two-stage serial batch testing program, in which leachates from representative ash samples were allowed to interact separately with relevant rock materials under laboratory conditions,
- Single-stage mixed batch testing program, in which 50:50 mixtures of the same ashes and rock samples were extracted with water following a similar procedure to leaching tests used for the individual ash and rock samples.

The concentrations of major and trace elements released in both studies were compared to the concentrations expected from the leaching characteristics of the individual ash and rock samples, when tested alone. In both the serial tests and the mixed-batch tests, these showed markedly lower concentrations of several key elements in solution (e.g. Mo, As, Se) after interaction of the ash leachate with the rock samples. The results indicate that some elements released from the ash in a mine backfill may be attenuated to a significant extent when the leachate comes into contact with other rock materials.

The attenuation properties appear to be related to the nature of the rock in question. Test programs of this type may provide a useful tool for assessing the potential impacts of placing different ashes in close association with relevant rock types in mine backfills and similar applications. Although testing for any individual site should also consider the design of the proposed backfill, the regional hydrogeology and the results of other site investigations, collection, and evaluation of data from one or both methods, may be of value in more fully understanding and predicting the environmental impact of ash-based mine backfill programs.

Precipitation of germanium from coal fly ash leachates

Fátima Arroyo, Constantino Fernández-Pereira, University of Seville, School of Engineering, Chemical and Environmental Engineering Department Camino de los Descubrimientos, Seville, Spain, 41092.

Pilar Coca, ELCOGAS S.A., 13500 Puertollano, Ciudad Real, Spain

Germanium is present in the fly ash of the 335-MW ELCOGAS IGCC power plant in Puertollano, Spain. Relatively high Ge-extraction yields (up to 86 %) were obtained using pure water, allowing a low cost and environmentally acceptable Ge recovery process from fly ash.

The valorisation of coal gasification fly ash was studied by leaching the fly ash with different aqueous solutions, followed by precipitation of trace amounts of Ge from the leachate with cetyl-trimethyl-ammonium bromide (CTAB) and catechol (CAT). The global reaction can be described as follows: 

\[
2C_{19}H_{39}N_2 + Ge(C_6H_4O_2)_4 \rightarrow Ge(C_6H_4O_2)_2 \cdot C_{19}H_{39}N_2 + 2C_{19}H_{37} \text{ (1)}
\]

The influences of pH and amount of CTAB and CAT on the precipitation yield were investigated. For an appropriate set of experiments, a statistical technique such as a response surface methodology (RSM) was used. A central composite rotatable design was employed for experimental design and analysis of the results. The precipitation yield was assessed by a quadratic model and the optimum values of these factors were found to be 10, 12, and 4, respectively. In this case, the Ge precipitation yield was 98.8% for water leachates.

The precipitation of Ge as an organic complex with CAT and CTAB was found to be selective towards Ge and this element can be effectively separated from As, Mo, Se, V or Zn, as can be seen in Table 1.

The content of Ni in the water leachate is virtually the same as Ge. The precipitation yields were high in all tests and, therefore, it could become an important interference in the precipitate. The order of interference of other metals is as follows: No → Zn → Mo → V → As.

Germanium precipitation is also possible from carboxyl leachates by adding only CTAB (87%). The main interference in this case is also Ni.

Total organic carbon was measured and results allowed estimation of the CAT and CTAB precipitated with Ge and interferences.

Thermo-gravimetric analyses performed to the Ge-complex solid revealed the following evolution:

1. From room temperature to 100°C the loss of water occurred.
2. In the range 180°C - 290°C, a 24.5% of mass was reduced.
3. The reduced mass in the second step was 19.0%.
4. The following step began at 340°C and the mass loss was 24.4%.
5. The last step began at around 500°C.
6. At constant weight, the roasted precipitate had 16.9% of the initial precipitate mass.

The precipitation of Ge as an organic complex with CTAB and CAT was found to be selective towards Ge and this element can be effectively separated from As, Mo, Se, V or Zn, as can be seen in Table 1.

<table>
<thead>
<tr>
<th>Leachate</th>
<th>Test no. 1</th>
<th>Test no. 8</th>
<th>Test no. 9</th>
<th>Test no. 10</th>
<th>Test no. 11</th>
<th>Test no. 17</th>
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<tbody>
<tr>
<td>mg/L</td>
<td>mg/L</td>
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<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
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<td>16.8</td>
<td>13.5</td>
<td>12.5</td>
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<td>15.2</td>
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<tr>
<td>Mo</td>
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<td>0.01</td>
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</tr>
<tr>
<td>Se</td>
<td>0.15</td>
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<tr>
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<td>0.28</td>
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<td>0.28</td>
</tr>
<tr>
<td>V</td>
<td>0.33</td>
<td>0.32</td>
<td>0.33</td>
<td>0.32</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>Ge</td>
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<td>76.1</td>
<td>76.1</td>
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<td>76.1</td>
</tr>
</tbody>
</table>

Taking into account this following mechanism for the decomposition of the Ge-complex is proposed:

\[
[\text{CTAB} \cdot \text{Ge}(\text{CAT})_2] \cdot [\text{Ge} \cdot \text{CAT}]_2 + 2 \text{CTAB} \rightarrow \text{T}=1180°C \ (2) \\
[\text{Ge} \cdot \text{CAT}]_2 + 2 \text{CAT} \rightarrow \text{T}=360°C \ (3) \\
[\text{Ge} \cdot \text{CAT}]_2 + \text{Ge} \cdot \text{CAT} \rightarrow \text{T}=340°C \ (4) \\
\text{Ge} + \text{O}_2 \rightarrow \text{GeO}_2 \ (5) \\
\text{GeO}_2 \ (\text{residue}) \rightarrow \text{T}=600°C \ (6)
\]

Full paper available at: www.coalgp-journal.org
Manufactured coal ash aggregates for aqueous TNT sorption

Sangchul Hwang, Victor Hernandez, Departmen of Civil Engineering, University of Puerto Rico, Mayaguez, PR

1. Introduction
Environmental contamination with high explosives, such as nitroaromatics (TNT) and dimers thereof, has been posing a significant threat due to their toxic effects to humans, animals, agricultural produce, and other natural receptors (Pires and Agathos, 2006). Coal combustion byproducts (fly and bottom ashes) have been utilized as sorption media for remediation of hazardous compounds (Asokan et al., 2015).

Manufactured coal ash aggregates (MAAs) are a solidified compo- site of fly and bottom ashes (2:1 by weight) that are mixed in water and then air-dried. They gain strength with time due to the hydration of the contained portlandite, which is the main chemical component of both fly and bottom ashes (2:1 by weight) that are mixed in water and then air-dried. They gain strength with time due to the hydration of the contained portlandite, which is the main chemical component of both (Peres and Agathos, 2000). Coal combustion byproducts (fly and bottom ashes) are known to be structurally stronger and chemically more stable (Pando and Hwang, 2000). This research was conducted to evaluate the potential of MAAs to adsorb or encapsulate the target contaminants, which is the purpose of this study. MAAs were mixed with a proper dilution.

2. Materials and Methods
2.1 Manufactured coal ash aggregates and TNT solutions
MAAs were sampled at a local coal-burning power plant in Puerto Rico as they were produced. The main chemical components of the MAAs were (silica + alumina + ferric oxides), lime, and sulfur trioxide, representing 51%, 30%, and 14.7% by weight, respectively. Prior to the use for the experiment, they were crushed mechanically and sieved to collect the particulate sizes in the range of 1.0 (US Sere Number 18) to 2.0 mm (US Sere Number 10). A standard TNT solution that was purchased from Restek Corp. and the initial target TNT concentration of 1 mg/L was made with a proper dilution.

2.2 Sorption kinetic and isotherm experiments
Sorption kinetic study was performed to assess an equilibrium time frame for the MAAs. The same amount of MAAs (2.5 g) were placed in several batch reactors and the same amount of TNT solution (12 mL) at 1.0 mg/L TNT was added to the reactors. The reactors were prepared in duplicate. They were kept in a slow speed end-over-end rotational shaker (ThermoE Labquake Shaker) at 8 rpm in order to facilitate contact between the MAAs and TNT molecules.

Sorption equilibrium experiments were performed using a similar technique. The MAAs were placed in a glass bottle and the initial concentration of 1 mg/L was added to the MAAs. The same MAAs were used in the kinetic experiments. The MAAs were stored in a 4°C refrigerator until the kinetic experiments were performed. In each kinetic experiment, the MAAs were placed in a glass bottle and the initial concentration of 1 mg/L was added to the MAAs. The same MAAs were used in the kinetic experiments. The MAAs were stored in a 4°C refrigerator until the kinetic experiments were performed.

2.3 Batch adsorption/TNT sorption
SBBR was treated as a reactor setup for TNT-contami- nated water with MAAs. Initially, 12 mL of TNT solution at a concentration of 1.0 mg/L was injected into a 20 mL glass cylinder reactor which had 2.5 g of the MAAs. After a one hour of contact time on the shaker, the finely-deposited liquid (~97% of the initial) was decanted from the reactor for the aqueous TNT analysis, but the spent MAAs were retained in the SBBR. Then, another 12 mL of TNT at 1.0 mg/L were

re-added to the SBBR and the system was shaken for another hour.

2.4 Analysis
The TNT concentration was measured with an HPLC (Pulkin Elmon Series 200). Aqueous samples taken at different time intervals were filtered with a 0.2-μm membrane filter. Sorption of the used membrane filter in acetonitrile solution and subsequent HPLC analysis showed no TNT rapped in membrane filter. The mobile phase of the HPLC was a mixture of methanol (MeOH) and deionized (DI) water at a ratio of 70% MeOH to 30% DI water at a flowrate of 1 mL/min. The HPLC column used was a Supelco C18 (25 cm x 6 mm x 5 μm). The UV lamp in the HPLC was set to a wavelength at 254 nm. One microliter of sample was injected to the HPLC with a detection limit of 0.2 μg/L TNT.

3. Results and Discussion
3.1 Sorption equilibrium time and isotherms
As shown in Figure 1, a pseudo-first order kinetics model was applied to achieve the goals, batch sorption properties than fly and bottom ashes in a sense that they are more structurally stronger and chemically more stable (Pando and Hwang, 2000). The Freundlich exponent (1/n) less than 1 implies the sorption to the MAs played a key role in TNT sorption to the MAs. To achieve the goals, batch sorption and isotherms tests and a sequencing batch sorption reactor (SBSR) were run at a laboratory scale.

3.2 Sequencing batch sorption reactor
To achieve the goals, batch sorption and isotherms tests and a sequencing batch sorption reactor (SBSR) were run at a laboratory scale.

3.3 Sorption kinetic data was modeled using pseudo-first order kinetics as follows (where kf represents the observed pseudo-first order sorption rate constant)

\[ q_k = k_f t^{1/n} \]

where \( q_k \) is the observed pseudo-first order sorption rate constant.

Sorption kinetic data was modeled using pseudo-first order kinetics as follows (where \( k_f \) represents the observed pseudo-first order sorption rate constant).

3.3.1 Freundlich sorption model
Freundlich sorption model is expressed as follows:

\[ q = K_f c^{1/n} \]

where \( q \) is the quantity of the TNT sorbed on the MAAs, \( c \) is the equilibrium concentration of the TNT in the liquid. The Freundlich constant \( K_f \) and \( 1/n \) were estimated using the Langmuir isotherm model.

3.3.2 Langmuir sorption model
Langmuir sorption model is expressed as follows:

\[ q = \frac{Q_m b c}{1 + b c} \]

where \( Q_m \) is the maximum sorption capacity and \( b \) is the sorption energy.

3.4 Freundlich exponent (1/n) less than 1 implies the sorption to the MAs played a key role in TNT sorption to the MAs. To achieve the goals, batch sorption and isotherms tests and a sequencing batch sorption reactor (SBSR) were run at a laboratory scale.

4. Summary
Pseudo-equilibrium sorption of TNT to the MAs was attained after 2 hours of contact time at a \( k_f \) of 0.05 min⁻¹. The Freundlich sorption model fit well the sorption isotherms data, with \( K_f \) being 25.7 mg/kg (L/mg)⁻¹/n and \( 1/n \) being 0.379. The MAs completely sorbed all the TNT up to the 3rd sequence of sorption in an SBBR where the application rate was 4.6 mg TNT/kg MAs per each cycle. The sorbed TNT was not desorbed from the MAAs under the given desorption conditions of this investigation.

5. Conclusion
Overall, the research presented in this manuscript shows that the MAAs could be used as sorption media for remediation of TNT-containing water. However, care should be given for their potential to introduce other contaminants to the aqueous phase with various environmental conditions (e.g., pH, hydrologic charac- teristics, and temperature), although the MAAs are already solidified aggregates and would not have secondary contamina- tion as much as fly and bottom ashes.

Acknowledgments
The authors appreciate the Research and Development Center at University of Puerto Rico at Mayaguez for financial sup- port through the New Faculty Seed Money Grant Program.

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Figure 1. Results from the sorption kinetic experiment. Data are the average of duplicate runs. Standard deviations were 3.5% range. A pseudo-first order sorption kinetic fit the data (eq 2).

Figure 2. Aqueous TNT concentration after each sequence of the SBSR. Data are the average of duplicate runs. Standard deviations were 3.5% range.

tnT concentration = 0.96 mg/L. Therefore, total 0.035 mg of TNT during three sequences completely sorbed to 2.5 g MAAs (i.e.,~ 14.4 mg TNT/kg MAs). The MAAs were not saturated with the TNT even after the 6th sequence. However, the residual TNT concentration of the SBSR was calculated to be 0.08, 0.09, and 0.12 mg/L after the 4th, 5th, and 6th sequence, respectively. These were corresponding to 91%, 90%, and 87%, respectively, of the TNT reduction by sorption. It should be noted that the SBSR was run for 1 hour of sorption contact time for each sequence. A shorter sorption contact time than aqueous equilibrium time could lead under- estimation of the extent of compound's sorption (Hwang and Carrige, 2004). Nevertheless, overall sorption capacity of the SBSR was calculated to be 28.8 mg TNT/kg MAs after completion of the 6th sequence. A blank SBSR system without the MAAs was also run and showed a minimal decrease (±2%) in TNT concentration at the end of the experiment. Aqueous TNT degradation was reported at high pH level greater than 11.0 via alkaline hydrolysis (Hwang et al., 2005). However, the reaction pHs were in the range of 9.5 to 6.5 throughout the sorption experiments. Therefore, it is assumed that the TNT alkylhydroxylide did not take place, but that the sorption to the MAAs played a key role in TNT reduction during the experiments.

Sorbed TNT was not desorbed out of the MAAs within 2 hours of desorption time. This could be attributed to a very slow rate of TNT desorption or an irreversible sorption of TNT to the MAAs (Hwang and Carrige, 2002). Further investiga- tion is warranted to elucidate the rate and mechanism of TNT desorption from the MAAs.
Manufactured coal ash aggregates for aqueous TNT sorption

Sangchul Hwang, Victor Hernandez, Department of Civil Engineering, University of Puerto Rico, Mayaguez, PR.

1. Introduction
Environmental contamination with high explosives, such as nitroaromatics (TNT) and dinitrotoluenes, has been posing a significant threat due to their toxic effects to humans, animals, agricultural produce, and other natural receptors (Pires and Agabian, 2000). Coal combustion byproducts (fly and bottom ashes) have been utilized as sorption media for remediation of hazardous compounds (Asokan et al., 2015). Manufactured coal ash aggregates (MAs) are a solidified compound formed from fly and bottom ashes (~2:1 by weight) that are mixed in water and then air-dried. They gain strength with time due to the structural strength and chemical stability of the fly ash (Pandol and Hwang, 2006). This research was conducted to evaluate the use of MAs as a treatment option for TNT-contaminated water and to study TNT sorption in contact with the synthesized aggregates.

2. Materials and Method
2.1 Manufactured coal ash aggregates and TNT solutions
MAs were sampled at a coal-burning power plant in Puerto Rico as they were produced. The main chemical components of the MAs were silica, calcium, alumina, felds, lime, and sulfur trioxide, representing 51%, 30%, and 14.7% by weight, respectively. Prior to use for the experiment, they were crushed mechanically and sieved to collect the particles sizes in the range of 0.15 mm to 0.3 mm (US Sieve Number 18) to 2.0 mm (US Sieve Number 10). A standard TNT solution that was purchased from Restek Corp. and the initial target TNT concentration of 1 mg/L was made with a proper dilution.

2.2 Sorption kinetic and isotherm experiments
Sorption kinetic study was performed to assess an equilibrium time for the sorption of TNT to the MAs. The same amount of MAs (2.5 g) were placed in several batch reactors and then the total amount of TNT solution (12 mL) at 1.0 mg/L TNT was added to the reactors. The reactors were prepared in duplicate. They were stirred on a lab scale, end-over-end rotational shaker (Thermolyne Labquake Shaker) at 8 rpm in order to facilitate contact between the MAs and TNT molecules. A replicate batch reactor was prepared using a different amount of the MAs (1.0 to 3.5 g) with the same volume (12 mL) at the TNT concentration of 1 mg/L and the initial target TNT concentration time obtained from the kinetic experiment aforementioned (i.e., 2 h) and at room temperature (i.e., 23 ± 1°C).

2.3 Sorption batch sorption reactor
SBSR was treated as a removal option for TNT-contaminated water with MAs. Initially, 12 mL of TNT solution at a concentration of 1.0 mg/L was filled in a 20 mL glass syringe reactor which had 2.5 g of the MAs. After a one hour of contact on the shaker, the freely-diluted liquid (~97% of the initial) was decanted from the reactor for the aqueous TNT analysis, but the spent MAs were remained in the SBSR.

As shown in Figure 1, pseudo-equilibrium TNT sorption to the MAs was assumed to be achieved after 2 hours of sorption equilibrium time. The initial aqueous TNT concentration of 1.0 mg/L was reduced to 0.02 mg/L after 2 hours of sorption contact time. It was repeated that the sorption equilibrium was achieved with the seven organoy adsorption within 2 hours (Upson and Burns, 2006). Sorption kinetic data was modeled using pseudo-first order kinetics as follows: where is the observed pseudo first-order sorption rate constant. The value of was calculated to be 0.05 min⁻¹ with a regression coefficient of R² = 0.91. For sorption isotherms, the TNT concentrations sorbed to the solids were plotted against the aqueous TNT concentrations.

The difference between the initial and final aqueous TNT concentrations was used for calculation of the TNT amount sorbed to the MAs. The blank system without the MAs were run simultaneously to assess any loss of TNT during the experiment. It showed ~2% loss of the TNT concentration after 2-hour experiment due probably to sorption to the reactor wall. Therefore, the reductions of TNT sorption in the sorption reactors were due to TNT sorption to MAs.

The sorption isotherm data was fit to Freundlich sorption model where is the equilibrium concentration of the compounds sorbed to the solids, is the Freundlich sorption constant, is the Freundlich exponent, and is the equilibrium concentration of the compound in liquid. The Freundlich constant was calculated to be 25.7 mg TNT/kg MAs with n = 0.379. The Freundlich exponent (n) less than 1 implies that TNT sorption to the MAs was favorable.

3. Results and Discussion
3.1 Sorption equilibrium time and isotherms
As shown in Figure 1, a pseudo-equilibrium of TNT sorption to the MAs was assumed to be achieved after 2 hours of sorption equilibrium time. The initial aqueous TNT concentration of 1.0 mg/L was reduced to 0.02 mg/L after 2 hours of sorption contact time. It was repeated that the sorption equilibrium was achieved with the seven organoy adsorption within 2 hours (Upson and Burns, 2006). Sorption kinetic data was modeled using pseudo-first order kinetics as follows: where is the observed pseudo first-order sorption rate constant. The value of was calculated to be 0.05 min⁻¹ with a regression coefficient of R² = 0.91. For sorption isotherms, the TNT concentrations sorbed to the solids were plotted against the aqueous TNT concentrations.

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Overall, the research presented in this manuscript shows that the MAs could be used as sorption media for remediation of TNT-contaminated water. However, care should be given for their potentials to introduce other contaminants under various environmental conditions (e.g., pH, hydrologic characteristics, and temperature), although the MAs are already solidified aggregates and would not have secondary contaminations as much as fly ash and bottom ashes.

Acknowledgments
The authors appreciate the Research and Development Center at University of Puerto Rico at Mayaguez for financial support through the New Faculty Seed Money Grant Program.

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