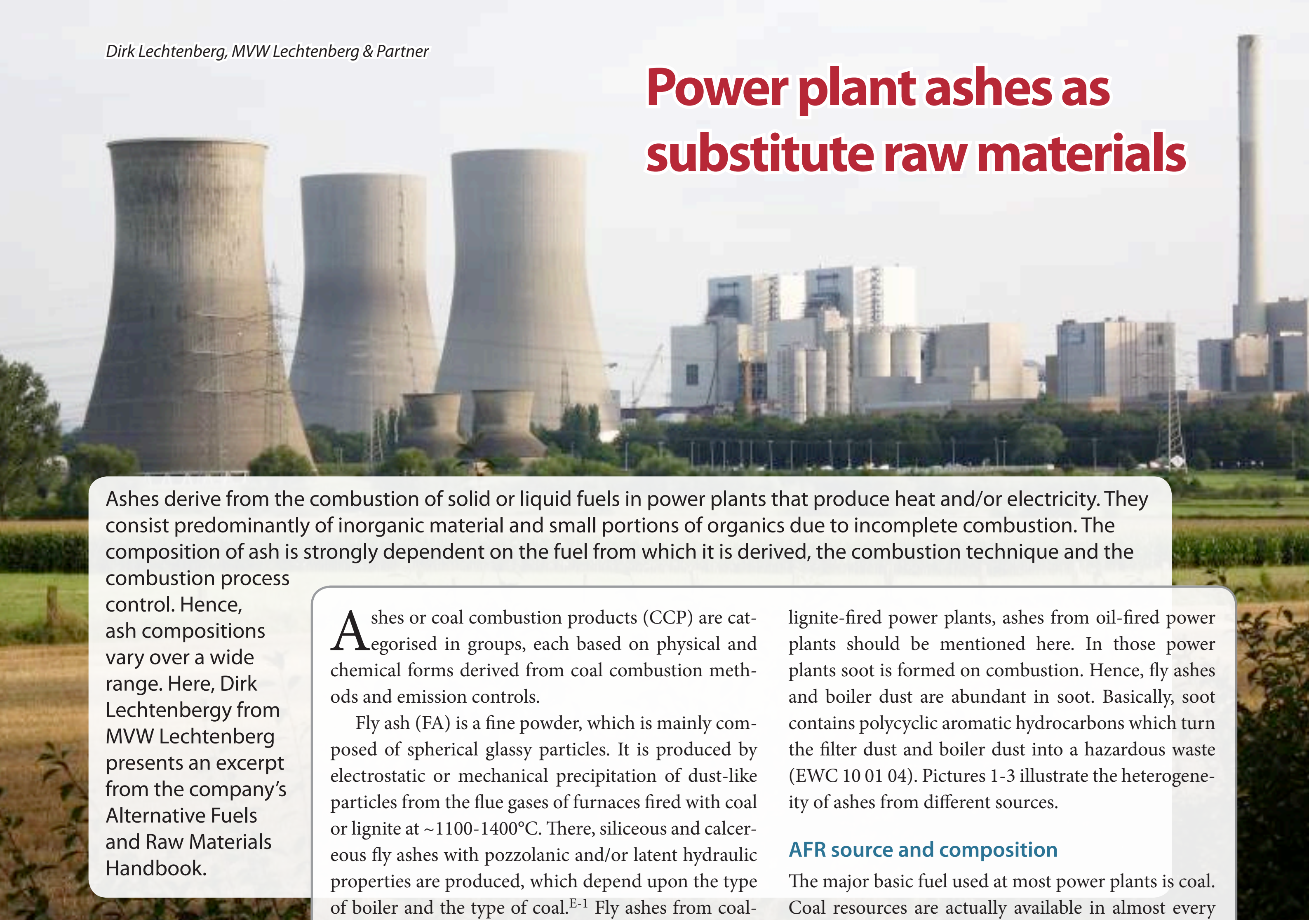
Dirk Lechtenberg, MVW Lechtenberg & Partner

Power plant ashes as substitute raw materials



Ashes derive from the combustion of solid or liquid fuels in power plants that produce heat and/or electricity. They consist predominantly of inorganic material and small portions of organics due to incomplete combustion. The composition of ash is strongly dependent on the fuel from which it is derived, the combustion technique and the combustion process control. Hence, ash compositions vary over a wide range. Here, Dirk Lechtenbergy from MVW Lechtenberg presents an excerpt from the company's Alternative Fuels and Raw Materials Handbook.

Above: A hard coal power plant: Cooling towers are on the left. The generator, boiler house and other facilities on the right.

Ashes or coal combustion products (CCP) are categorised in groups, each based on physical and chemical forms derived from coal combustion methods and emission controls.

Fly ash (FA) is a fine powder, which is mainly composed of spherical glassy particles. It is produced by electrostatic or mechanical precipitation of dust-like particles from the flue gases of furnaces fired with coal or lignite at ~1100-1400°C. There, siliceous and calcereous fly ashes with pozzolanic and/or latent hydraulic properties are produced, which depend upon the type of boiler and the type of coal.[E-1] Fly ashes from coal-fired power plants can be categorised into European Waste Code (EWC) 10 01 02.

On the other hand, (furnace) bottom ash (BA) is a granular material removed from the bottom of dry boilers. This is much coarser than FA though also formed during the combustion of coal.

Further, boiler slag (BS) is a vitreous grained material deriving from coal combustion in boilers at temperatures of 1500-1700°C. This process is followed by wet ash removal of wet bottom furnaces. Bottom ashes and slag can be categorised into EWC 10 01 01.

Fluidised bed combustion (FBC) ash is formed in fluidised bed combustion boilers. This technique combines coal combustion and flue gas desulphurisation in the boiler at 800-900°C. This material can be categorised by EWC 10 01 24.

Although the focus of this article targets coal or lignite-fired power plants, ashes from oil-fired power plants should be mentioned here. In those power plants soot is formed on combustion. Hence, fly ashes and boiler dust are abundant in soot. Basically, soot contains polycyclic aromatic hydrocarbons which turn the filter dust and boiler dust into a hazardous waste (EWC 10 01 04). Pictures 1-3 illustrate the heterogeneity of ashes from different sources.

AFR source and composition

The major basic fuel used at most power plants is coal. Coal resources are actually available in almost every country worldwide. Coal provides 30.3% of global primary energy needs and generates 42% of its electricity. In 2011 coal was the fastest growing form of energy outside renewables.[W-1]

The top ten coal and lignite producers along with their coal production quantities in 2011 are displayed in the Figures 1 and 2. Indeed, many countries rely virtually fully on coal as an energy source. In other countries coal represents a significant proportion besides other sources such as nuclear energy.

According to a report from the International Energy Agency[F-1] the globally installed coal-fired power plant fleet consists of approximately 1627GW generating capacity in total (2010). Over the last five years, net power generating capacity increased from coal-fired power plants, in particular for large power plants above 300MW capacity.

Below - Picture 1: Wet ash from a German lignite power plant.

Below centre - Picture 2: Wet ash from a German hard coal power plant.

Below right - Picture 3: Fly ash from a hard coal power plant.

More than 20% of the currently installed facilities worldwide is younger than five years and more than 50% of the installed facilities younger than 20 years. Just 10 countries represent more than 85% of the world's total CO_2 emissions from coal or peat through the production of electricity and heat.

Quantity and availability

In 2007 China had the largest coal ash production followed by India and Europe. By that time, the total production of coal ashes attained an estimated 720Mt.[B-1] This is divided into: **China:** 300Mt (est.); **North America:** 95Mt; **India:** 105Mt; **Europe:** ~111Mt; **Russia:** 25Mt; **South Africa:** 31Mt; **Japan:** 11Mt; **Other countries:** ~42Mt.[B-2]

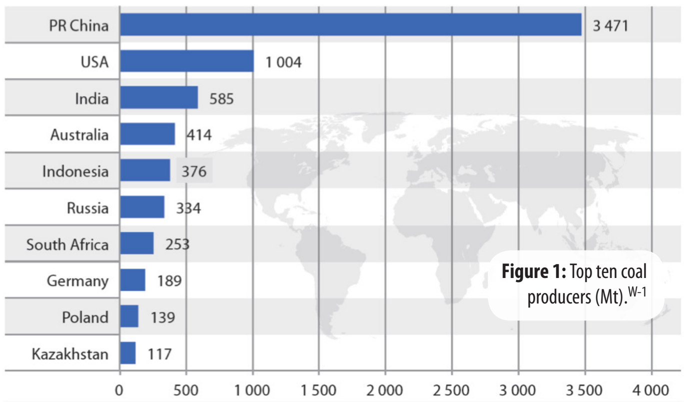


Figure 1: Top ten coal producers (Mt).[W-1]

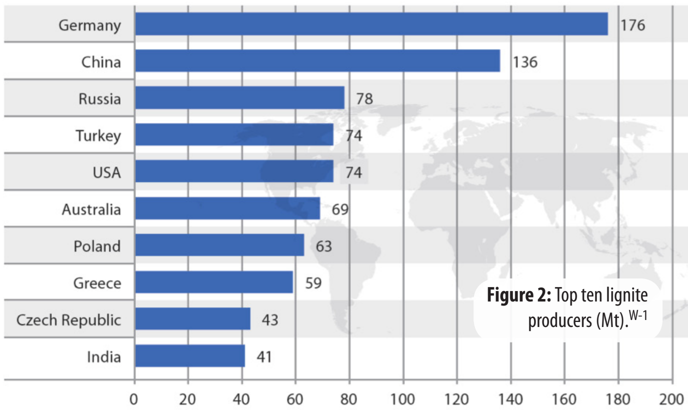


Figure 2: Top ten lignite producers (Mt).[W-1]

Owing to the constant need for electricity power plants normally work around the clock. Downtime phases occur a couple of weeks per year owing to maintenance of boilers, turbines and other facilities. By and large ashes are available continuously over the whole year.

Composition

Ash composition varies over a wide range. The following tables provide examples of different kinds of ashes.

Fly ashes are classified as Class C or Class F according to ASTM C 618.[A-1] Class C fly ash, also referred to as high-calcium fly ash, is normally produced by burning lignite or sub-bituminous coal. Class F fly ash, also referred to as low-calcium fly ash, is generally produced by burning anthracite or bituminous coal.

Class C fly ash usually has cementitious properties in addition to pozzolanic properties which can be traced back to free lime. Class F fly ash is rarely cementitious when mixed with water alone.

Recycling, current use and disposal

Coal ashes are used in a wide range of applications in the building and construction industry. In most cases the materials are used as a replacement for naturally occurring resources and therefore offer environmental benefits by removing the need to quarry or mine such natural resources.

Coal ashes also help to reduce energy demand as well as emissions to atmosphere, for example CO_2. Such applications include usage as an additive in concrete as cement replacement material and as an ag-

Below right - Table 1: Chemical composition of typical bottom ash.[N-1]

Component	Bituminous coal	Sub-bituminous coal
SiO_2	61.0	46.8
Al_2O_3	25.4	18.8
Fe_2O_3	6.6	5.9
CaO	1.5	17.8
MgO	1.0	4.0
Na_2O	0.9	1.3
K_2O	0.2	0.3

Above right - Table 2: Chemical composition of typical boiler slag in percent.[N-1]

Component	Bituminous coal	Sub-bituminous coal
SiO_2	48.9	40.5
Al_2O_3	21.9	13.8
Fe_2O_3	14.3	14.2
CaO	1.4	22.4
MgO	5.2	5.6
Na_2O	0.7	1.7
K_2O	0.1	1.1

Right - Table 3: Chemical composition of fly ashes and requirements for cement usage in percent.[N-1]

Component	Class F fly ash		Class C fly ash	
	Typical	ASTM C-618 requirements	Typical	ASTM C-618 requirements
SiO_2	53.6	N/A	40.9	N/A
Al_2O_3	26.3	N/A	21.6	N/A
Fe_2O_3	5.2	N/A	5.5	N/A
All of the above	90.2	>70	67.7	>50
CaO	4.1	N/A	19.1	N/A
MgO	1.5	N/A	3.9	N/A
SO_3	0.9	<5.0	1.4	<5.0
Loss on ignition	6.0	6.0	6.0	6.0
Moisture	0.2	<3.0	0	<3.0
Insoluble residue	0	N/A	0	N/A
Na_2O equivalent	2.0	N/A	1.6	N/A

Left - Picture 4: Fly ash loading facility for lorries in a lignite-fired power plant.

The use of high-carbon fly ash in raw kiln feed has the additional benefit of saving fuel. For instance, in a wet-process plant, a fly ash containing 15% carbon and fed at 15% raw feed replacement will save around 150kCal/kg of clinker.

In a dry process plant, at a 10% replacement level, it could save nearly 10% of the total fuel energy.[B-4] However, if the carbon volatilises at a lower temperature than is used for burning, the emission of volatile organics could increase. For this reason the usage of such ashes for raw mill grinding might be restricted for suspension preheater kilns in countries which have TOC emission limits. However, if high-carbon fly ash is used for raw meal preparation in older LEPOL kilns, TOC might be not an issue. Injecting the fly ash directly into the burning zone would prevent this problem.

In a wet-process operation, high carbon fly ash can cause the segregation of carbon particles which may float on top of the slurry. The use of a Class C fly ash would result in thickening of the slurry and may necessitate additional water or a slurry thinner to maintain the required flowability.[B-4]

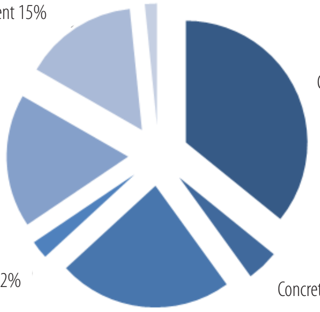
gregate or binder in the road construction industry. It is also used in mineral fillers and as fertiliser.[E-2]

Figure 3 shows the utilisation of fly ash in the construction industry and in underground mining in 2008 in the EU.

Use as alternative raw material in cement production

Clinker: Fly ash from coal-fired power plants can be used effectively as a component of raw kiln feed for the manufacture of cement clinker. Fly ash contains significant amounts of Al_2O_3 and SiO_2 and has thus been used as a partial replacement of natural raw materials like clay and/or shale in the raw kiln feed. In some cases the Fe_2O_3 content of the fly ash has also provided iron balance in the raw feed. Hence, natural iron ore can also be saved.

Fly ash can be used in both dry and wet cement manufacturing. In the dry process the fly ash is either premixed with the raw kiln feed or introduced directly into the burning zone. The resulting clinkers have shown sufficient homogeneity although some inhomogeneities in the clinker phases have been observed when the fly ash is introduced directly into the burning zone. In the wet process, the fly ash is added to the slurry. The level of addition is dependent upon the fly ash composition and the behaviour of the slurry.



Left -Figure 3: Use of fly ash in industry in 2008.

Owing to the large amount of silica and aluminium oxide, other ashes such as boiler ash, fluidised bed combustion ashes, bottom ashes can be used as a silica and alumina carrier for raw meal production. They partially contain carbon from incomplete combustion of coal in power plants.

Wet boiler ashes can be used, after drying, in a circulating fluidising bed reactor along with other alternative combustibles in order to produce lean gas which is used in a calciner. Once the ashes leave the circulating fluidising bed reactor they can be used without prior treatment as a raw material for raw meal production.

Cement

Fly ashes are used as pozzolanic materials for cement production. The fly ashes have to fulfil certain criteria. ASTM International[A-1] classifies fly ash into two categories—Class F and Class C.

Class C fly ash, also referred to as high-calcium fly ash, is normally produced by burning lignite or sub-bituminous coal. Class F fly ash, also referred to as low-calcium fly ash, is generally produced by burning anthracite or bituminous coal.

ASTM C 618 distinguishes Class C fly ash from Class F fly ash on the basis of the total SiO_2, Al_2O_3 and Fe_2O_3 content:

Class F fly ash: $SiO_2 + Al_2O_3 + Fe_2O_3 > 70\%$.
Class C fly ash: $50\% < SiO_2 + AlO_3 + Fe_2O_3 < 70\%$.

Some Class C fly ashes contain sufficient CaO themselves to be sufficiently cementitious. The permitted proportions of fly ashes in cements are regulated by corresponding cement standards.

Fly ashes also find markets in concrete manufacturing. There are strong requirements to be fulfilled when using fly ashes for concrete buildings. For instance, the European standard EN 450 Fly Ash for Concrete describes the provisions for fly ashes.

Economic value of the AFR in a cement plant

CCP's contain significant amounts of Al_2O_3 and SiO_2. They can substitute natural raw materials such as clay and/or shale in the raw kiln feed. In some cases the Fe_2O_3 content is also high. Hence, natural iron ore can be saved. Owing to the wide variety of chemical composition of CCPs it is impossible to provide certain substitution factors. Each substitution case has to be evaluated individually.

When fly ash is used to displace clinker in Portland cement there are two main benefits. Firstly, aluminosilicates in the ash react with calcium hydroxide, augmenting its cementitious properties and increasing the strength and durability of the final product. Secondly, Portland cement production releases high amounts of CO_2. But for every tonne of fly ash used in replacement, one tonne of CO_2 emission is also avoided. This could be a major element of an overall greenhouse gas reduction strategy.[N-1]

Quality influence on clinker and cement

CCPs high levels of Al_2O_3 and SiO_2 (and occasionally Fe_2O_3) also influence the lime saturation factor, alumina ratio and silica module. Owing to the wide variation in chemical compositions of CCPs it is not possible to predict the influences on the modules. Each case has to be evaluated individually.

Fly ash-containing cements display some special features: Good workability thanks to the ball-shaped fly ash; Lower heat generation compared to ordinary Portland cement OPC, therefore less cracks in solid concrete; Lower early compressive strength and comparable late compressive strength compared to OPC and; Less tendency to blooming.

Summary

The use of ashes from coal fired power plants can reduce the CO_2 emissions in the cement industry significantly. Ash usage is a common practice already in many countries but still has huge potential, especially in the Middle East and north African region, south east Asia and the Americas.

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