

# Coal Fly-Ash Utilisation in Greece

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## ABSTRACT

Significant economic and environmental problems coming from the disposal of coal ash have led to the implementation of various alternative uses, in which combustion residues are considered as value-added products. In Greece, a large quantity of fly-ash is the inevitable by-product of Greek brown coal burning, due to its high ash content. In this paper, the main characteristics of fly-ash from Greek coal-fired boilers are presented in relation to its exploitation potential. Both fuel and fly-ash samples were collected and analysed according to the ASTM Standards. Apart from the typical analyses (proximate, ultimate, ash analysis and calorific value), an ICP-AES spectrometer was used for the analysis of heavy metals in the ash. Experimental measurements in order to determine the radioactivity content of raw fuel and the fly-ash were carried out as well. The ashes from the Greek brown coal are classified in type C, e.g. into class with high proportion of CaO, due to the fact that compounds of sulphur – calcium – aluminates are predominant. The total annual fly-ash production for the last two years was about  $10 \times 10^6$  tons, most of which are produced in Ptolemais, Northern Greece. Ptolemais fly-ash is rich in calcium compounds, while Megalopolis fly-ash contains more pyrite. Increased heavy metal concentrations are observed in the fly-ash samples of Greek coal. Greek fly-ash appears to have not only pozzolanic but also hydraulic behaviour. Furthermore, Greek fly-ash, depending on its origin, may have relatively high natural radioactivity content, reaching in the case of Megalopolis fly-ash  $1 \text{ kBq kg}^{-1}$  of  $^{226}\text{Ra}$ . Fly-ash is mostly used in Greece in cement industry replacing cement clinker and aiming to the production of special types of Portland cements. However, a more aggressive utilization strategy should be developed, since low quantities of the total produced fly-ash is currently further utilized.

KEYWORDS: Greek fly ash, chemical analysis, radioactivity, utilisation.

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## 1. INTRODUCTION

A large quantity of fly ash is the inevitable by-product of Greek lignite burning, due to its high ash content. The total annual ash production for the last two years was about  $10 \times 10^6$  tons, of which  $7.6 \times 10^6$  tons are produced in northern part of Greece and  $2.4 \times 10^6$  tons in southern part of Greece (Megalopolis). Greek fly ash appears to have not only pozzolanic but also hydraulic behaviour<sup>1</sup>. Ashes are mostly used in Greece in cement industry replacing cement clinker and aiming to the production of special types of Portland cements. The cement companies bought almost 7-15% of these quantities, over the last decade. Moreover, they were successfully tested in road construction, several mortars, waste treatment, embankments and cement grouting. However, an unremarkable progress in large utilisation of fly ash in cement still prevails and is mainly attributed to the high transportation cost, as well as to the lack of norms covering their utilisation. Although significant advantages derived from the use of fly ash, the addition in large quantities of fly ash as supplementary material in concrete in Greece is delayed due to (a) the variations in the chemical and mineralogical composition, (b) the necessity for supplementary grinding of ashes in order to reveal their pozzolanic and hydraulic properties, (c) the high proportion of its free CaO, and (d) the periodically high proportions of SO<sub>3</sub> content. A more detailed study of fly ash properties is required towards the enhancement of its utilisation in the aforementioned applications.

The main objective of the paper is to present the results from an in-depth analysis on the main features of Greek fly ash and examine its potential uses. Apart from the theoretical work to predict the fly ash quantities in the next decade, several laboratory methods were applied in order to characterise this by-product. Recommendations about future fly ash utilisation options are the main outcome of all research efforts.

## 2. METHODOLOGY

**Potential of fly ash utilisation in Greece:** A theoretical model to estimate the produced fly ash quantities and its exploitation in some selected routes - since detailed data on all possible routes are not available – was used<sup>2</sup>. The resources savings associated with these fly ash utilization options were estimated.

The annual production of fly ash ( $A_{fa}(t)$ ) in the forthcoming years depends on (1) gross electricity generation based on coal, (2) overall power plants thermal efficiency, (3) coal calorific value and (5) coal ash content. It can be calculated (in million tones) as follows<sup>2</sup>:

$$A_{fa}(t) = f_3 f_4 \beta G(t) / n UHV \quad (1)$$

Major areas of fly ash utilisation are (a) making of bricks/blocks, cellular concrete products and lightweight aggregates, (b) manufacture of cement and asbestos, (c) road construction and (d) embankment, backfill, land development, etc. Other potential sectors include the asbestos production, cellular concrete products, lightweight aggregates, backfill materials, land development, etc. The present analysis considers fly ash utilization in cement production, brick manufacture and construction of road embankment, since these routes can accommodate a major

portion of produced ash. The amount of fly ash used in these options in any specific ( $t$ -th) year is estimated through the following equations<sup>2</sup>:

Cement production:

$$A_{fa-PPC}(t) = f_6 f_7 A_{cement}(t) / \{1 + [(f_6/f_5) - 1] \exp[(1/T) \ln(0.002f_5)/(f_6 - f_5)]\} \quad (2)$$

Brick manufacture:

$$A_{fa-brick}(t) = N_{brick}(t) d_{cb} [f_{10} + \{(f_{11} - f_{10})/T\}t] V_{brick} \Sigma(e_j s_j) \quad (3)$$

Road embankments:

$$A_{fa-emb}(t) = R(t) [f_{12} + \{(f_{13} - f_{12})/T\}t] [\{(SW+H)/S\}H] d_{soil} F_1 \quad (4)$$

Fly ash utilization would lead to savings in natural resources, mainly the land (and soil), water, coal and limestone. Large-scale utilization of fly ash in the manufacture of bricks and the construction of road embankments would release considerable amounts of land. In total, the land (in hectares) to be saved from fly ash use is expressed:

$$L_{total}(t) = L_{brick}(t) + L_{ash\ pond} + L_{emb}(t) \quad (5)$$

Water will be saved due to reduced fly ash disposal from power plants and equals to:

$$Q(t) = \{[U_{fa}(t) A_{fa}(t)] / d_{fa}\} SPC_{water}, \quad (6)$$

PPC production will lead to reduced coal consumption as well as savings in limestone due to reduced clinker requirements:

Coal savings:

$$C_{PPC}(t) = [A_{fa-PPC}(t)/f_7] \{(SPC_{th1} - SPC_{th2}) + [(SPC_{el1} - SPC_{el2}) (1/nUHV)]\} \quad (7)$$

Limestone savings:

$$LS_{PPC}(t) = (A_{fa-PPC}(t)/f_7) (SPC_{OPC} - SPC_{PPC}) (100/56) \quad (8)$$

**Ash production:** The Greek coal-fired power plants consist of six thermal stations with a total capacity 4,898 MW<sub>e</sub>. All lignite-fired power units use pulverised coal combustion conventional technology. The pollutant emissions for the Greek lignite-fired power plants are presented in Table 1. Lignite combustion for power generation accounts for about half of the emissions of sulphur dioxide, while it is estimated that about 2282 tons of fly ash / MW / year is produced in average. All Greek lignites are characterised by low heating value, high initial moisture, and high ash content, while Megalopolis lignite is characterised by its high sulphur content. Typical average analysis of Ptolemais and Megalopolis reserves are shown in Table 2. Ptolemais reserves represent the main deposit currently under exploitation in Greece, contributing with ~45% of the total Greek lignite deposits. Furthermore, its quality characteristics seem to be representative for the majority of Greek lignite reserves. Therefore, the main body of tests was conducted with samples from Ptolemais reserves. Apart from the typical analyses (proximate, ultimate, ash analysis and calorific value), an ICP-AES spectrophotometer was used for the analysis of heavy

**Table 1.** Pollutant Emissions from Lignite-Fired Power Plants, 2000.

<b>Power Plant</b>	<b>Capacity (MWe)</b>	<b>SO<sub>2</sub> (gram/GJ)</b>	<b>NO<sub>x</sub> (gram/GJ)</b>	<b>Particulates (gram/GJ)</b>	<b>Ash (tons/MW- year)</b>
<b>Agios Dimitrios</b>	1595	160	148	66	2297
<b>Kardia</b>	1225	160	134	54	1797
<b>Ptolemais</b>	620	178	32	36	2030
<b>Amynteo</b>	600	588	75	33	2640
<b>Megalopolis</b>	850	2621	115	159	2650
<b>Total emissions in 2000</b>		249.8 kt	47.1 kt	28.2 kt	

Source: Ministry of Development

metals in lignite ash, since some these heavy metals are of environmental interest and may affect pore structure development.

**Ash characterisation:** A variety of standard methods for fly ash characterisation exist. The uses of fly ash define the significant parameters (physical, chemical and mineralogical properties), which should be determined. Thus, the related characterisation methods are mainly included in the standards governing the utilisation of fly ash. According to these standards and norms, fly ash is classified in relation to the content of its major elements (Si, Al, Fe and Ca). ASTM C 618 defines three classes: (a) Class N which includes raw or calcinated natural pozzolans with at least 70% SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, (b) Class F comprising ash produced from anthracite or bituminous coal combustion with at least 70% SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, (c) Class C comprising ash produced from lignite or sub-bituminous coal combustion with at least 50% but less than 70% SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, Class F fly ashes usually contain less than 5% CaO, while fly ashes belonging to Class C contain a large proportion of CaO (10 – 35%). On the other hand, EN 197-1 classifies fly ashes in two types, siliceous V (less than 10% CaO) and calcareous W (10 – 35% CaO). Based on the above, fly ashes originated from the combustion of Greek lignites are classified to calcareous W (EN 197-1) or to Class C (ASTM C 618) due to their high CaO content that reflects the ash composition of the parent lignite. A major problem concerning the utilisation of fly ash is the variability of its chemical behaviour, because of the different coal, the degree of pulverisation, the temperatures in the furnace during combustion, and finally the methods of the collection and handling. These factors differ from one power plant to another, resulting to different fly ashes. The variability in fly ash is mainly attributed to the different combustion conditions and less to the inorganic content of the parent fuel. The most significant physical and chemical properties and parameters when using fly ash are particle morphology, fineness, specific gravity, pozzolanic activity, pozzolanic activity index, accelerated pozzolanic activity index, soundness, reactivity with cement alkalis, initial setting time, water requirement, loss on

**Table 2.** Average characteristics of Ptolemais and Megalopolis lignites.

Analysis	Ptolemais	Megalopolis
<b>Proximate analysis, % w/w</b>		
Moisture	59.9	54.3
Volatiles	17.6	18.9
Fixed carbon	13.9	11.1
Ash	8.6	15.7
<b>Ultimate analysis, % w/w (dry ash free basis)</b>		
C	65.5	60
H	5.3	5
N	2.1	2
S	1.2	6
O (by subtraction)	25.9	27

ignition (carbon content), free CaO, total oxides, sulphur trioxide, moisture, magnesium oxide and available alkalis.

Mineralogical characterisation is valuable in determining the glassy and crystalline phases of fly ash. X-ray diffraction (XRD), energy dispersive X-ray analysis (EDXA), and scanning electron microscopy (SEM) studies of fly ash is commonly called mineralogical analysis of fly ash<sup>3</sup>. It is considered valuable in determining the crystalline phases that contain the major constituents of fly ash, “the element speciation”. Fly ash mineralogical characteristics are mostly dependent on the type and composition of the parent coal. The most variable phases identified in fly ash are anhydrite (CaSO<sub>4</sub>), periclase (MgO), magnetite, hematite, melinite and lime (CaO)<sup>3</sup>. Fly ashes yielding from the combustion of Greek lignites are characterised as Calcialic-Calcic. They contain a high percentage of glassy phase (20-40 %) which is related to pozzolanic properties and the high percentage of (CaO) which is responsible for the hydraulic properties<sup>4,5</sup>.

**Radioactivity measurements:** Lignite, like all minerals, contains natural radionuclides from the Uranium and Thorium series, as well as <sup>40</sup>K. These nuclides will therefore be present in fly and bottom ash, and their activity concentration should be determined prior to using the ash in other applications. Determination of the radioactivity content of fly ash can be accomplished using gamma spectrometry, with a minimum of sample preparation and good sample throughput. Other techniques, such as alpha spectrometry can also be applied. However, their use for the analysis of fly ash is in most cases not justified, as they are labour intensive and costly, while the activity levels found in fly ash are usually easily and accurately determined by gamma spectroscopy.

The Uranium series nuclides that are most often determined by gamma spectrometry are <sup>238</sup>U, <sup>226</sup>Ra and <sup>210</sup>Pb. Uranium 238 is determined via its daughter <sup>234</sup>Th, while <sup>226</sup>Ra is determined via <sup>214</sup>Pb, <sup>214</sup>Bi, daughters of <sup>222</sup>Rn. These measurements require that the parent and daughter

nuclides be in radioactive equilibrium, having equal activities. This is achieved by storing the sample for an appropriate time span prior to measurement – a few months in the case of  $^{238}\text{U}/^{234}\text{Th}$  equilibrium, or a few weeks for  $^{226}\text{Ra}/^{222}\text{Rn}/^{214}\text{Pb}/^{214}\text{Bi}$  equilibrium. If  $^{226}\text{Ra}$  is to be measured, the samples must also be sealed to prevent the escape of gaseous  $^{222}\text{Rn}$ .

Similarly, of the nuclides in the Thorium series,  $^{228}\text{Ra}$  is determined via  $^{228}\text{Ac}$  and  $^{228}\text{Th}$  is determined via  $^{212}\text{Pb}$  and  $^{208}\text{Tl}$  using gamma spectrometry. Radioactive equilibrium must be established in this case also, but the delays involved are much shorter – a few days for  $^{228}\text{Ac}$  – but the need for sealing of the samples also applies. The Thorium series is usually assumed to be in radioactive equilibrium down to thoron ( $^{220}\text{Rn}$ ); thus only one activity value for the series parent  $^{232}\text{Th}$  is quoted.

Gamma spectrometry in a laboratory environment is practically always performed using high resolution, high efficiency Ge semiconductor detectors. In recent years large detectors, with relative efficiency exceeding 100%, and detectors sensitive to low energy photons have become increasingly available. Such detectors are very well suited to the task of determining the activity concentration of gamma-emitters in fly ash, provided that appropriate calibration methods are applied.

Besides natural radioactivity content, radon exhalation from fly ash is another issue of interest. Radon isotopes  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$ , which are constantly produced by the decay of  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  respectively, require special consideration, as they are gaseous; a fraction of the radon produced will be exhaled from lignite and ash. Their activity in air is usually determined with dedicated instruments, based on standard nuclear measurement principles, such as ionization chambers. The parameter that is usually evaluated for radon emitting materials is the *exhalation rate*, i.e. the amount of radon released to the environment per unit time. It may be quoted on a mass basis, in the case of bulk materials, or on an area basis for materials such as building blocks.

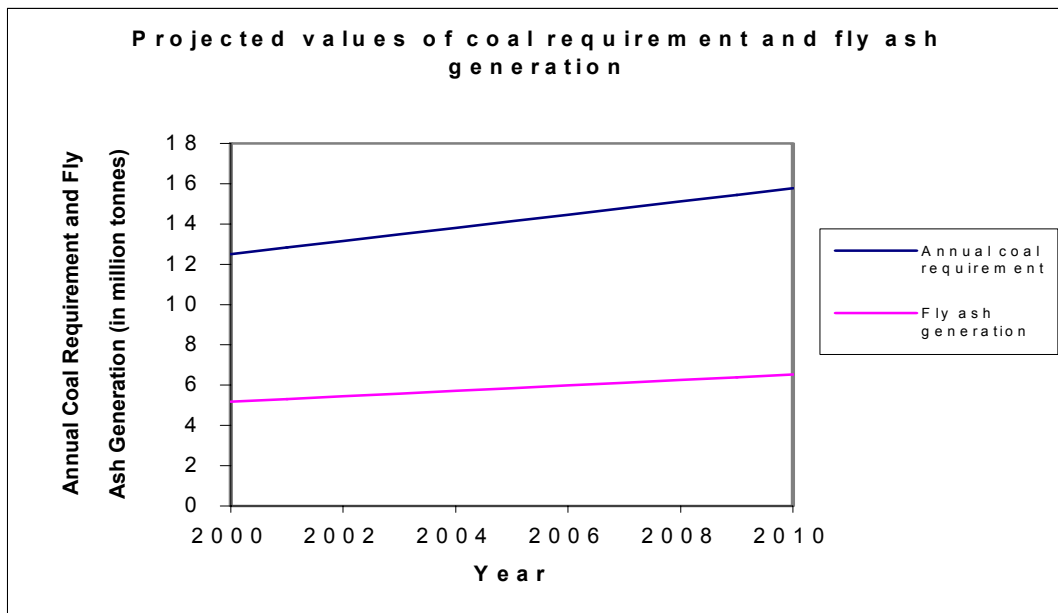
In cases where ash is used on a large scale, such as road construction, where guidelines for acceptable radioactivity levels do not exist, laboratory analyses should be supplemented with *in situ* gamma spectrometry and dosimetry. *In situ* spectrometry can be performed using Ge detectors, similar to those used in a laboratory setting, while basic dosimetry can be performed with simpler, appropriately calibrated instruments.

### 3. RESULTS AND DISCUSSION

**Ash quantities and uses in Greece:** Analysis methodology included forecast up to year 2010 of annual gross electricity generation, coal consumption and fly ash production, Figure 1. Projected values up to year 2010 of annual cement production, number of manufactured bricks and incremental road length were estimated also, Table 3. Three scenarios were developed, based on the assumption that after 5, 10 or 15 years the 50% of cement production will be Portland Pozzolana Cement (PPC), and fly ash will be used for the 10% of produced bricks and in the 20% of incremental road length. Quantitative estimation of fly ash utilisation up to 2010 was realised for each case and resources savings were evaluated then, Figure 2. Cement production can adsorb large amounts of fly ash, since its annual production is estimated around 15 Mtn

today, Table 3. Fly ash can be used in the production of Portland Pozzolana Cement (PPC) in three different ways: (1) as a raw material along with limestone in the cement kiln, (2) in grinding of fly ash and cement in the mill and (3) in blending of Ordinary Portland Cement (OPC) with fine fly ash. The most important application of coal fly ash in Greece was implemented in 1992, when the Greek Public Power Corporation went forward with the construction of Platanovryssi dam, applying the RCC technique and utilising fly ash, coming from Ptolemais Power Station, as basic cementitious material. Since then, several tests have been made for ensuring the suitability of fly ash for the construction of the dam. A total amount of about 140,000 tones of milled fly ash has been used up today for the project. From the experience gained till now, as well as from the thousands of tests which have been performed, it is concluded that lignite ash is a cheap raw material of satisfactory properties, which, when properly blended with cement, can be utilised for the construction of various technical projects. A considerable amount of fired clay bricks is manufactured in the country, estimated at around 300 Mtn per year, Table 3. The bricks are used primarily for the construction of houses and other civil works. National and state highways are often constructed on raised embankments and soil is normally used for this purpose. Fly ash utilisation in the construction of road embankments is very promising, as incremental road length is considered to be about 375 km, Table 3.

Fly ash utilisation will lead to savings in natural resources, Table 4, mainly in land (soil), water, coal and limestone<sup>6-9</sup>. Large-scale utilisation of fly ash, especially in the manufacture of bricks and the construction of road embankments, will release considerable amounts of land. It may lead to reduced land/soil requirements for (1) ash ponds, (2) clay brick production and (3) the construction of road embankments. Water will be saved due to reduced fly ash disposal from power plants. Moreover, thermal and electrical energy required for PPC production is less than

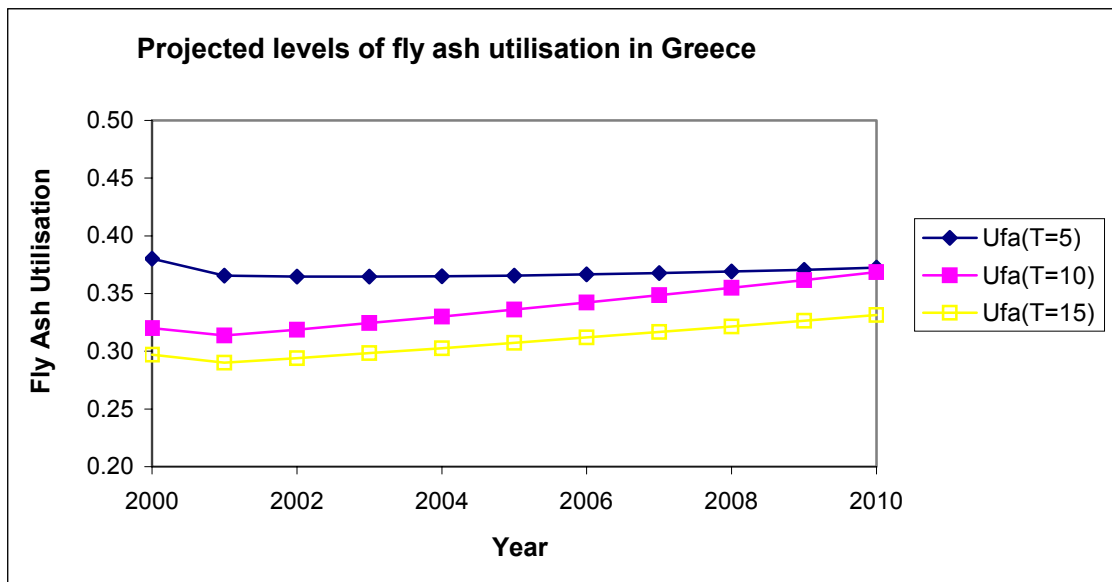


**Figure 1.** Projected values of coal requirements and fly ash generation.

**Table 3.** Projected values of cement production, brick manufacture and incremental road length.

Year	Cement (million tones)	Brick (million tones)	Road length (km)
2000	15.46	87.3	356
2001	14.92	420.4	367
2002	15.01	310.8	377
2003	15.10	312.4	388
2004	15.19	314.1	398
2005	15.27	315.7	409
2006	15.36	317.3	419
2007	15.45	319.0	430
2008	15.53	320.6	440
2009	15.62	322.3	451
2010	15.71	323.9	461

that required for the production of OPC. Since coal is used as the source of energy production in cement plants, substantial coal savings may arise. Finally, PPC production would lead to reduction of limestone requirements in the process of clinker production. The above show that about 70% of total amount of utilised fly ash is absorbed in PPC production, considerable amount of land would be saved due to reduced fly ash storage requirements. In all cases, the overall fly ash utilisation remains less than 40% of total produced quantities, and therefore, a more aggressive utilisation strategy has to be developed.



**Figure 2.** Projected levels of fly ash utilization in Greece.

**Ash properties:** The average chemical analyses of Ptolemais and Megalopolis fly ashes are given in Table 5, regarding major and minor elements. As anticipated calcium oxide dominates in fly ash obtained from Ptolemais power plants, Table 5, due to the increased Ca content of the

raw coal, Table 2. The sum of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> of Ptolemais fly ash is ~60% and, thus, it is classified as Class C. Alumina and silica oxides are the major compounds in Megalopolis fly, Table 5, ash reflecting the composition of the parent coal, Table 2. For Megalopolis fly ash the sum of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> exceeds 70% (~74%) and thus it is classified as Class N. Minor elements that could be of environmental concern are given in Table 5 also and for both fly ashes no extreme values were observed.

**Radioactivity:** Greek lignite is known to contain increased activity concentration levels of the Uranium series radionuclide <sup>226</sup>Ra<sup>10-25</sup>. Representative values found in the literature for the activity concentration of <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K of lignite mined at various Greek lignite fields are presented in Table 6. The values for <sup>226</sup>Ra are significantly higher than the worldwide reference levels given by UNSCEAR<sup>17</sup>, while <sup>232</sup>Th and <sup>40</sup>K activities are generally within the expected ranges. Since most radionuclides are enriched in the fly ash as compared to the original lignite<sup>25</sup>, it is expected that Greek fly ash will also have increased radioactivity. Fortunately, because of the high ash content of Greek lignites, enrichment ratios are lower than those reported in higher quality coals.

Several researchers have studied the radioactivity content of Greek fly ash<sup>10, 12-16, 18-21</sup>. Values reported are presented in Table 7. Fly ash from Greek power plants, and ash originating in the Megalopolis power plant in southern Greece in particular, does indeed contain significant levels of <sup>226</sup>Ra activity, which in some cases may even exceed 1000 Bq kg<sup>-1</sup>. Similarly to Greek lignite, Thorium series activities are considerably lower in fly ash, while the radioactivity of <sup>40</sup>K is generally comparable to values reported for western power plants<sup>12, 26</sup>.

It should be noted that fly ash, even when coming from a single power plant, is not homogeneous with respect to radioactivity content. This is in part due to the variability of activity concentrations in lignite, even within a single seam, as well as variations in the power plant operating parameters. Furthermore, significant variations have been observed between samples of fly ash collected at different points within a single power plant<sup>15,16,25,26</sup>; physical and chemical processes taking place along the flue gas pathway as well as size fractionation of the fly ash at the different sampling points are believed to be the cause of these variations.

Radioactive equilibria are usually disturbed in fly ash, with parent and daughter nuclides having unequal activities. Values ranging from 0.89 to 1.37 have been reported for the <sup>238</sup>U/<sup>226</sup>Ra ratio in the case of Megalopolis fly ash<sup>16</sup>, while the <sup>210</sup>Pb/<sup>226</sup>Ra ratio shows even greater variation, ranging from 0.63 to 3.47. Both of these facts imply that when assessing fly ash from a radiological perspective concerning its possible utilisation one should be careful to (a) use representative samples of fly ash, preferably collected at the end user's ash supply and (b) avoid making assumptions about radioactive equilibrium to deduce the activity concentration of parent nuclides from their daughters and vice versa.

Some investigation of the radon exhalation rates of Greek fly ash has been performed<sup>16</sup>. Values reported for Megalopolis fly ash range from 12 to 117 μBq kg<sup>-1</sup> s<sup>-1</sup>, and were found to correlate well with the fly ash particle size distribution. It should be noted that the exhalation rate for fly ash was found to be significantly lower than that for Megalopolis lignite, reaching up to 266 μBq kg<sup>-1</sup> s<sup>-1</sup>.

**Table 4.** Projected resources savings (coal, limestone, land and water).

Year	Resources saved											
	Coal (thousand tonnes)			Limestone (thousand tonnes)			Land (hectares)			Water (million m <sup>3</sup> )		
	T=5	T=10	T=15	T=5	T=10	T=15	T=5	T=10	T=15	T=5	T=10	T=15
2000	106	89	82	1.9	1.6	1.5	2020	1860	1700	24.60	20.7	19.2
2001	102	86	79	1.8	1.5	1.4	2050	1880	1720	24.3	20.8	19.3
2002	103	86	80	1.8	1.5	1.4	2080	1890	1730	24.8	21.7	20.0
2003	103	87	80	1.8	1.5	1.4	2110	1910	1740	25.4	22.6	20.8
2004	104	87	81	1.9	1.6	1.4	2140	1930	1750	26.1	23.6	21.6
2005	105	88	81	1.9	1.6	1.5	2180	1950	1760	26.8	24.6	22.5
2006	105	88	82	1.9	1.6	1.5	2220	1970	1770	27.4	25.6	23.3
2007	106	89	82	1.9	1.6	1.5	2250	1980	1790	28.1	26.7	24.2
2008	106	89	82	1.9	1.6	1.5	2290	2010	1800	28.9	27.8	25.2
2009	107	90	83	1.9	1.6	1.5	2330	2030	1820	29.6	28.9	26.1
2010	108	90	83	1.9	1.6	1.5	2380	2050	1830	30.4	30.1	27.1

**Table 5.** Average chemical analyses of Ptolemais and Megalopolis fly ashes.

Major elements (% w/w)			Trace elements (ppmw)		
Compound	Ptolemais	Megalopolis	Element	Ptolemais	Megalopolis
SiO <sub>2</sub>	33.4	47.7	As	7	20
Al <sub>2</sub> O <sub>3</sub>	13.1	18.5	Be	2.1	1.5
Fe <sub>2</sub> O <sub>3</sub>	5.6	7.9	Cd	0.9	1.7
CaO	31.9	14.9	Cr	199	60
MgO	4.5	2.7	Co	20	38
K <sub>2</sub> O	1.2	1.7	Cu	60	32
Na <sub>2</sub> O	0.8	0.8	Pb	14	20
SO <sub>3</sub>	6.8	3.9	Mo	6	13
			Ni	155	80
			Se	1.1	2.2
			Sr	325	76
			V	117	192
			Zn	67	83

**Table 6.** Radioactivity content of Greek lignites.

Lignite Field	Sample Size	<sup>226</sup> Ra	<sup>232</sup> Th	<sup>40</sup> K	Ref.
(Mean ± s.d., in Bq kg <sup>-1</sup> dry mass)					
Achlada	3	407 ± 13	74 ± 3.0	411 ± 23	12
Amyntaio	5	33 ± 14	15 ± 3.7	96 ± 24	12
Kardia	5	174 ± 19	16 ± 1.5	67 ± 15	12
Megalopolis	5	314 ± 52	21 ± 2.0	181 ± 26	13
	5	321 ± 40	21 ± 1.0	191 ± 14	13
Ptolemais	5	85 ± 7.4	15 ± 1.5	78 ± 15	12
Vevi	2	204 ± 41	26 ± 11	196 ± 89	12
Worldwide typical ranges		10-25	10-25	50-110	17 25

**Table 7.** Radioactivity content of Greek fly ashes.

Source	Sampling Location	<sup>226</sup> Ra	<sup>232</sup> Th	<sup>40</sup> K	<sup>238</sup> U	<sup>210</sup> Pb	Ref.
(Bq kg <sup>-1</sup> ± 1σ uncertainty)							
<b>Aliveri</b>		307 ± 33	1.3 ± 0.44		529 ± 122		18
<b>Kardia</b>	ESP B	500			640		20
	Unit I – ESP	600 ± 74	49 ± 5.18	218 ± 18,5			12
	Air Preheater	192			340		20
	ESP A	337			481		20
		385 ± 33			868 ± 124		10
		385 ± 33	7.1 ± 0.52		858 ± 122		18
<b>Megalopolis</b>	Unit III – ESP	845 ± 71	56 ± 1				13
	Unit I – ESP	807 ± 138	55 ± 2				13
	ESP	747 ± 96	67 ± 7.3		60 ± 12		21
	Unit IV – Economiser	863 ± 60	56 ± 2.8	508 ± 35	771 ± 54	538 ± 340	16
	Unit IV – ESP	904 ± 81	52 ± 1.04	454 ± 50	964 ± 67	1158 ± 127	15
	Unit IV – Air Preheater	869 ± 99	57 ± 3.4	520 ± 36	794 ± 79	539 ± 481	16
		392 ± 33	7.1 ± 0.96		492 ± 122		18
	Cement manufacturer	800 ± 200	54 ± 10	290 ± 120			19
		392 ± 33			496 ± 124		10
<b>Ptolemais</b>		422 ± 30			508 ± 124		10
	Cement manufacturer	330 ± 20	53 ± 4	190 ± 30			19
	Unit IV – ESP	263 ± 19	45 ± 15	252 ± 15			12

The question of the suitability of fly ash for use in the cement industry, taking its radiological properties into account, was raised as soon as these properties were investigated for the first time. Initial dosimetric estimations concluded that the use of fly ash cement should be avoided to limit exposure to radiation, or at least confined to structures such as foundations and open-air public works<sup>10</sup>. However, subsequent studies reached different conclusions<sup>19,21,22</sup>, suggesting that fly ash may be used in cement to a considerable extent, and called for the development of regulations for the radioactivity content of building materials.

A group of Experts appointed by the European Commission recently made some progress towards developing uniform regulations for the radioactivity content of building materials, reported in Radiation Protection Document 112 of the European Commission<sup>24</sup>. Due to the cost and practical difficulties of thoroughly assessing the dose rates at each specific building constructed, the group of experts suggested that the following Radiation Protection Index (RPI) be used to identify building materials that may lead to an unacceptably high dose rate and require further investigation:

$$RPI = C_{Ra} / 300 \text{ Bq kg}^{-1} + C_{Th} / 200 \text{ Bq kg}^{-1} + C_K / 3000 \text{ Bq kg}^{-1}$$

Where  $C_{Ra}$ ,  $C_{Th}$  and  $C_K$  are the  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  activity concentrations in  $\text{Bq kg}^{-1}$ . The RPI has been introduced based on conservative estimates for model buildings, and has been designed to cover both direct gamma exposure as well as exposure to Radon. It is assumed that both the Uranium and the Thorium series will be in equilibrium in building materials. These estimates suggest that materials used in bulk, such as concrete, are unlikely to lead to dose rates higher than  $0.3 \text{ mSv a}^{-1}$  and may be used without further investigation when the RPI is less than 0.5.

To provide a qualitative estimate of the suitability of Greek fly ash for use in cement, we have used data presented in Table 7 to calculate the maximum amount of fly ash that can be substituted in typical Greek cement, under the constraint that  $RPI < 0.5$  for the resulting concrete. The results of these calculations are presented in Table 8. It can be seen that Ptolemais and Kardia fly ash may be used without restriction, while Megalopolis fly ash may be used in amounts up to 70%, exceeding those actually used in practice (20-30%). Although these results may be overly optimistic, since radioactive disequilibrium is known to exist in fly ash and thus the RPI should strictly not be used, the qualitative conclusion that can be drawn is that, from a radiological point of view, Greek fly ash can safely be used in concrete to a considerable extent. However, measurements of the fly ash actually used for cement manufacturing should be performed, as activity levels may vary.

Some radioactivity measurements have been performed on Greek cement containing fly ash as an additive<sup>19, 27-30</sup>. The values reported for  $^{226}\text{Ra}$  range from 29 to 160  $\text{Bq kg}^{-1}$ . The Radon exhalation rate of concrete blocks containing fly ash has also been measured, and found to range from 210 to 3000  $\mu\text{Bq m}^{-2} \text{ s}^{-1}$ <sup>19, 27-29</sup>.

**Table 8.** Estimated maximum permissible fly ash fraction in cement, based on the RPI.

Fly ash source	$^{226}\text{Ra}$	$^{232}\text{Th}$	$^{40}\text{K}$	Maximum ash fraction
	( Bq kg <sup>-1</sup> )			
<b>Kardia</b>	600	49	218	100%
<b>Megalopolis ESP</b>	904	52	454	68%
Air Preheater	869	57	520	70%
Economiser	863	56	508	71%
<b>Ptolemais</b>	263	45	252	100%

#### 4. CONCLUSIONS

A simple framework for estimation of fly ash utilisation potential in Greece has been used. Fly ash utilisation in cement production, construction of road embankments and manufacture of bricks has been considered. The results obtained for the projected levels of fly ash utilisation clearly show that in spite of assuming quite optimistic levels of fly ash use in the three applications, the overall fly ash utilisation is less than 40% of the total fly ash produced. Therefore, either a much more aggressive fly ash utilisation strategy has to be developed and executed or the extent of the fly ash utilisation target (or the year of achieving a specified target) should be reviewed. Fly ash from both Ptolemais and Megalopolis area could be effectively used in Portland Pozzolane Cement, in bricks production and the construction of road embankments. Trace elements of environmental concern have not appeared in extreme concentrations.

Although Greek fly ash is known to contain increased radioactivity levels, particularly  $^{226}\text{Ra}$ , studies show that it can be safely used in cement in reasonable quantities. However, more detailed investigation of the issue should be performed, as results so far indicate that radioactivity levels in fly ash may vary considerably, depending on the sampling location within the power plant. For uses other than in the cement industry, little investigation of the radiological aspects has so far been performed; this is not surprising, as these uses are limited in Greece. In situ investigation of the dose rates and radionuclide mobilization in some cases, such as the Platanovryssi dam, would be particularly relevant.

## 5. NOMENCLATURE

Symbol	Unit	Value
$d_{cb}$	$\text{kg/m}^3$	1770
$d_{fa}$	$\text{kg/m}^3$	800
$d_{soil}$	$\text{kg/m}^3$	1100
$e_j$	fraction	0.5
$f_1$	fraction	885/24.289
$f_2$	fraction	827/24.289
$f_3$	fraction	0.8 (1989-1997)
$f_4$	fraction	0.9
$f_5$	fraction	0.4
$f_6$	fraction	asymptotic value of $f_5$
$f_7$	fraction	0.2 (maximum 30%)
$f_8$	fraction	0.7 (average value)
$f_9$	fraction	0.05
$f_{10}$	fraction	0.01
$f_{11}$	fraction	0.1
$f_{12}$	fraction	0.05
$f_{13}$	fraction	0.2
$F_1$	Factor	0.3
$g_i$	%	0.2 (1995-2000)
$H$	m	1
$H_{dyke}$	m	15
$j$	types of brick	2 (in equal qualities)
$n_V$	$\text{m}^3$	60 (four rooms considered for an average size house)
$R_1$	ratio	0.75
$s_j$	fraction	(a) 0.25, (b) 0.60
$S$	slope	1 in 2
$SPC_{water}$		10:1
$SPC_{th1}$	kg/tone of cement	233
$SPC_{th2}$		222
$SPC_{el1}$	kWh/tone of cement	118
$SPC_{el2}$		75
$SPC_{OPC}$	fraction	0.85
$SPC_{PPC}$	fraction	0.96
$T$	years	5, 10, 15
$UEL$	years	10
$UHV$	MJ/tone	7733
$V_{brick}$	$\text{cm}^3$	22.9cmx11.2cmx7.0cm
$W$	m	7
$Y$	persons per house	3.0
$Z$	m	1.5
$\beta$	%	46 %
$n$	efficiency	0.35

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