Mineralogical and chemical properties of FGD gypsum from Florina, Greece

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Abstract

BACKGROUND: The aim of this work is to define the chemical and mineralogical composition of the fuel gas desulphurization (FGD) gypsum produced from the Meliti thermal power plant in the region of Florina in North West Greece, in order to investigate potential uses in the cement industry. Mineralogical and microprobe analyses were carried out on FGD gypsum samples collected from the Meliti 330 MW lignite-fired power plant.

RESULTS: Results show that the main component of the FGD gypsum is pure mineral gypsum ($CaSO_4{\cdot}2H_2O$). The particle size of the gypsum ranges from 5 to 50 μm and the crystals are mainly of rhomboid shape. Microprobe analysis shows that the concentration of CaO and SO_3, which are the main components, range from 31.9%–32.5% and from 45.90–46.40%, respectively.

CONCLUSION: This FGD gypsum can easily substitute the natural gypsum used in the production of cement.

Keywords: petrography; SEM; FGD gypsum; X-ray diffraction

INTRODUCTION

In 2001 the European Commission introduced the 2001/80/CE Directive regarding atmospheric emission limits for SO_2, NO_x and dust from coal-fired power plants.[1] One of the ways of limiting emissions is by Fuel Gas Desulphurization (FGD) and such technologies can be divided into wet and dry processes, referring to the nature of the sorbent (reagent) when it leaves the absorber.

In Greece, the Public Power Corporation has relatively recently applied the wet process of limestone–gypsum desulphurization to reduce SO_2 emitted from the lignite-fired power plants of the Meliti power plant in the Florina region of north-west Greece and the Megalopolis power plant in the Peloponnesus region in south Greece. The Megalopolis FGD system has been in operation for several years whereas the Florina FGD system was recently installed in 2003. Both systems have performed under the same operational conditions and therefore the efficiency factor in both plants is identical.

The annual production of FGD-gypsum from these two power plants is estimated at around 1 Mt. Currently there is no commercial use for this FGD by-product and so it is currently used in combination with fly ash, for mine reclamation, to fill in openings that are left following the completion of mining activities.

The Florina (Meliti) power plant (Fig. 1) is located in north-west Greece, in the vicinity of Florina and close to the frontiers with the former Yugoslavian Republic of Macedonia (FYROM). The capacity of the lignite-fired power plant, which has been in operation since 2003, is 330 MW.

In the wet FGD limestone desulphurization process installed in the Meliti power plant, initially the fly ash is removed from the combustion gases and then the flue gas comes in contact with the alkaline slurry in a spray tower, where the acidic flue gases react with the dissolved alkali. Limestone, consisting of 96% calcite, 3% feldspars, and 1% quartz, is used as the adsorbent at a concentration of approximately 30 wt% solids, while the particle size distribution is 90% $< 44\,\mu m$.

The alkaline reagent reacts with the SO_2 converting it to sulphite:

$$CaCO_3 + SO_2 + H_2O \rightarrow CaSO_3{\cdot}0.5\,H_2O + CO_2 + 0.5\,H_2O$$

air is introduced into the reaction tank to oxidize the sulphite to sulphate:

$$CaSO_3{\cdot}0.5\,H_2O + 0.5\,O_2$$

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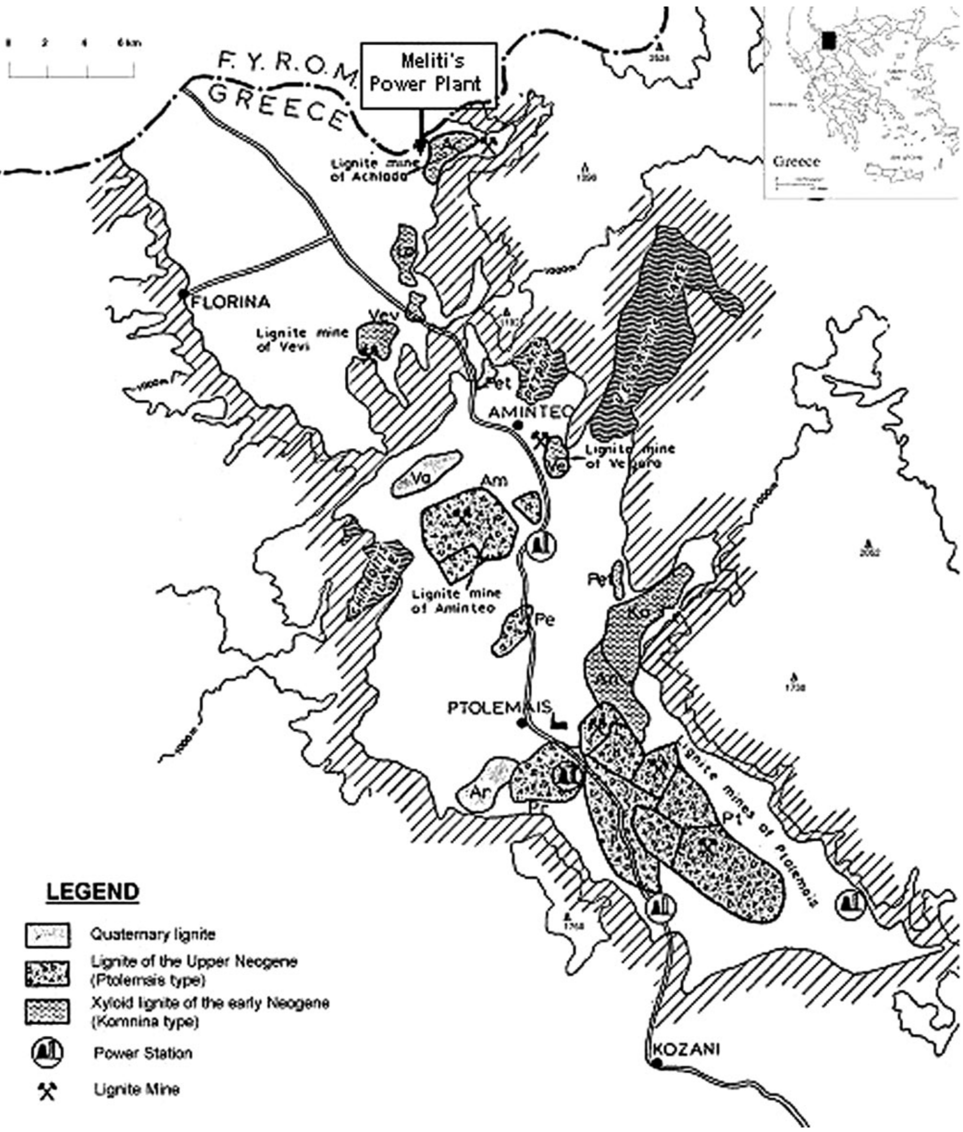

Figure 1. Location of the Florina (Meliti) lignite-fired power plant from where the FGD gypsum was collected. The lignite deposits and mines of the wider area of Ptolemais-Florina are also indicated (Pt = Ptolemais, Pr = Proastio, Ar = Ardassa, Ko = Komnina, An = Anatoliko, Pel = Pelargos, Pe = Perdikas, Am = Amynteon, Va = Valtonera, Ve = Vegora, Pet = Petres, Vev = Vevi, Lo = Lofi, Ac = Achlada).

$$+ 1.5\ H_2O \rightarrow CaSO_4 \cdot 2\ H_2O$$

This by-product is continuously bled from the reaction tank using hydrocyclone pumps.

Primary dewatering of gypsum is carried out by hydrocyclones with underflow 45–55% suspended solids and overflow <3% suspended solids, then secondary dewatering of gypsum is performed by vacuum belt filters yielding a filter cake with 10–12 wt% maximum moisture content. All the filtrates return to the reaction tank.

The Melita FGD plant has a removal efficiency for SO_2 and SO_3 of 97% and 50% respectively whereas the outlet value of SO_2 emissions is 400 mg $N^{-1}\ m^{-3}$ (dry).

FGD by-products are used in various applications throughout the world, with around 8.9 Mt of FGD by-products used in the USA,[2] which is of course part of the total FGD production (FGD gypsum, FGD material wet scrubbers, FGD material dry scrubbers, FDG other) which accounted for 30 Mt in 2003. The majority of FGD by-products are used in the cement, agriculture and wallboards industries (Table 1). In addition, other applications of FGD by-products are in mining and as stabilizing agents for wastes. In Europe (EU-15), the production of FGD by-products, mainly gypsum, was estimated[3] at more than 11 Mt, with their main use in the wallboard industry (Table 1).

Researchers have also reported the utilization of FGD by-products to control soil pH,[4,5] where it

Table 1. FGD gypsum utilization in USA and EU

	USA[a]	EU[b]
Cement	5.10%	42.30%
Wallboards	93.70%	51%
Agriculture	0.40%	
Concrete and concrete products	0.80	6.70%

[a] 2003.[2]
[b] Reference 3.

was proven that soil properties were improved and production increased by adding FGD by-products. FGD gypsum reacts with ammonium carbonate in an aqueous solution to produce ammonium sulphate fertilizer, which is a source of nutrients for plants.[6]

In Greece, gypsum is used in the production of cement, along with limestone, clays, pozzolana, and fly ash. Gypsum acts as retarder in cement production and is added in clinker to produce Portland cement.

The Greek cement market is appropriate for FGD gypsum, as the gypsum currently used often comes either from quarries in Crete or other places in Greece that are far from the cement production plants, or else the gypsum is imported. In other European countries, such as Spain, even though large amounts of FGD gypsum are produced from thermal power plants, as there are natural gypsum deposits in the country the use of FGD material is not often considered.

Taking into consideration the above applications, it is considered worthwhile to examine possible applications of Greek FGD by-products.

COMPOSITION OF FUEL

The Meliti power plant is fuelled by an xylitic type lignite from the nearby open-cast mines. Approximately 80% of the lignite is supplied from a private mine with the remainder from a mine belonging to the Public Power Corporation of Greece. The Achlada-Meliti deposit is of Lower Pliocene age with the characteristics shown in Table 2.[7] In addition to the Achlada-Meliti lignite mine there are three more deposits of xylitic lignite in the wider area of Florina. The characteristics of these Vevi, Lofi-Meliti and Klidi deposits are also shown in Table 2. The proven reserves of lignite are over 400 Mt while the economically recoverable reserves are estimated at around 200 Mt.[8]

The xylitic lignite was deposited during the Lower Neogene period and is interbedded with Miocene sediments consisting of sand, silt, clays, siltstone, sandstones and marls. Consequently the mineralogical and chemical composition of xylitic lignites, which feed the power plant, show great fluctuations. Furthermore, diatomite rocks and phosphatic nodules have been detected not only in the interbedded but also in the overburden sediments.[9] Two different layers that contain diatomaceous rocks can be recognized above the xylitic layers. Diatoms with a high calcium content can be detected in the first layer while high silica and alumina content diatoms are included in the second layer. The main minerals included in these layers are calcite, albite, chlorite, illite, muscovite, kaolinite, cristobalite and quartz. Phosphatic nodules have also been detected within the diatomite beds. In particular, high concentrations of P_2O_5 have been reported due to the presence of vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$) in the coal deposits of Klidi and Vegora.

Table 2. Analysis of Florina lignite (Achlada-Meliti, Vevi, Lofi-Meliti and Klidi deposits)[7]

Deposit	Calorific Value kJ/kg[a]	Ash (%)[b]	Moisture (%)[c]	Sulphur (%)[d]
Achlada-Meliti	8450	33.9	43.2	0.41
Vevi	9740	28.6	39.8	0.32
Lofi-Meliti	8440	30.4	45.4	0.41
Klidi	8530	28.9	44.9	0.76

[a] Net calorific value, on as received basis.
[b] On dry basis.
[c] On as received basis.
[d] Combustible sulphur, on as received basis.

Materials and methods

Representative samples of FGD gypsum were collected on two different days from the gypsum storage system of the Meliti power plant. After splitting into fractions, each sample was analysed by means of X-ray diffractometry (XRD), scanning electron microscopy (SEM) and inductively coupled plasma spectroscopy (ICPS). The mineralogical analysis was carried out by using a Siemens D-5005 X-ray powder diffractometer, with copper radiation and graphite monochromatographer. The mineralogical phases were determined by computer using SOCABIM (DIFRAC PLUS 2004, EVA version 10) software and the JCPDS files.

Microprobe analysis, grain size distribution and the mineral chemistry of the FGD gypsum were determined by SEM using a JEOL JSM-5600 and an OXFORD LINK ISIS 300 EDS. Microprobe analysis was carried out on two representative gypsum crystals from each sample (total four analyses).

The XRD and microprobe analyses were carried out in the Laboratory of Economic Geology, Department of Geology and Geo-Environment, University of Athens.

The bulk sample analyses of the FGD were carried out in the Laboratory of the Centre for Research and Technology Hellas in Thessaloniki using inductively coupled plasma–optical emission spectroscopy (ICP-OES) following digestion of the sample in HCl (37%) heated to 100 °C for 2 h.

RESULTS

Mineralogical composition

Mineralogical analysis of the FGD gypsum was carried out by XRD and SEM and the results of the XRD study are shown in Fig. 2. The main mineral phase gypsum is pure, fine grained, mineral gypsum, $CaSO_4{\cdot}2H_2O$ and in addition, albite ($NaAlSi_3O_8$) and quartz (SiO_2) were detected by SEM.

Bulk sample analysis

The chemical composition of the synthetic gypsum (Table 3) indicates a high proportion of CaO and SO_3 in FGD gypsum from the Florina power plant. These

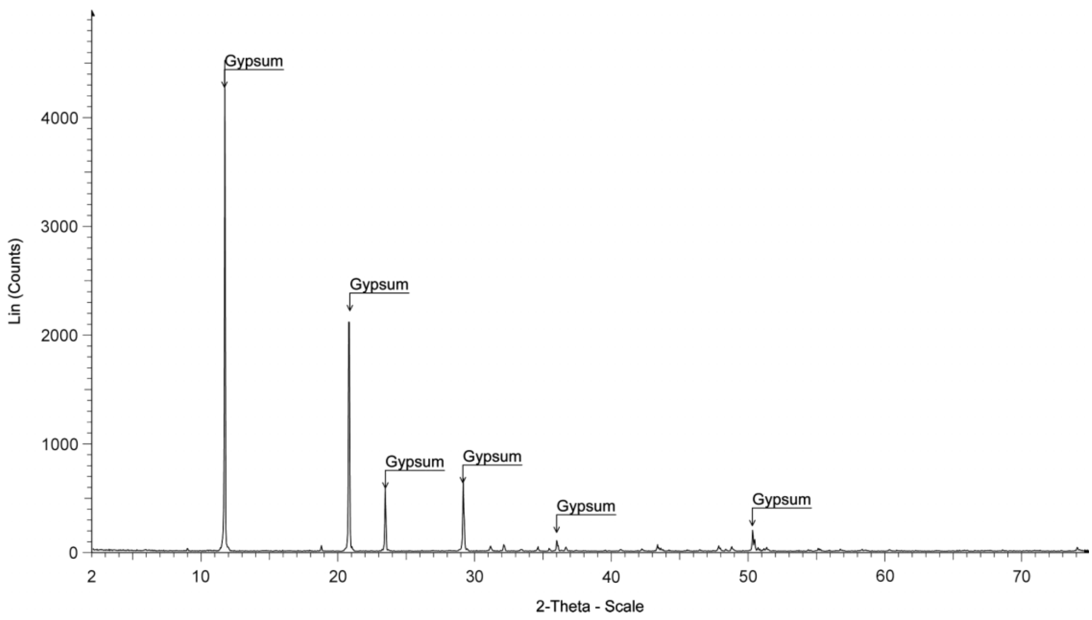

Figure 2. X-ray diffraction pattern of the Florina's FGD gypsum indicating the purity of gypsum.

Table 3. Major element composition (%) of Florina FGD (FFGD) gypsum, as determined by acid digestion and ICP-OES compared with typical composition of US FGD gypsum

Elements	FFGD Mean Values	Analytical accuracy	Standard Deviation	USA FGD Gypsum[a]
SiO_2	ND[b]			0.1–6.3
Al_2O_3	0.10	±0.01	0.01	0.1–5.1
Fe_2O_3	0.12	±0.01	0.01	0.1–5.7
CaO	32.63	±0.41	0.23	27–32
MgO	0.60	±0.07	0.03	1.0–4.9
Na_2O	ND[2]			0–0.6
K_2O	0.04	±0.01	0.01	0–0.6
SO_3	46.59		0.33	44–46
H_2O	19.77		0.45	

[a] Typical chemical composition of FGD gypsum in USA.[10]
[b] Not detected.

Table 4. Trace element composition (ppm) of Florina FGD gypsum (FFGD), as determined by acid digestion and ICP-OES, and the concentration range of trace elements in gypsum for cement production (GCP).[16]

Elements	FFGD Mean values	FFGD Analytical deviation	FFGD Standard deviation	GCP Min.	GCP Max.	GCP Average
As	<2.5[a]			0.2	3.5	1.5
Cd	<0.001[a]			0.03	2.3	0.1
Cr	<4[1]			1.0	27.3	8.8
Cu	3.79	0.08	1.1	0.3	12.8	7.0
Mn	26	2	0			
Mo	3.5	0.6	0.1			
Ni	<4[a]			0.3	14.5	5.5
Pb	<20[a]			0.20	20.5	7.0
Se	<5[a]					
V	2.2	0.08	0.5	1.0	27.8	13.5
Zn	26	8	15	1.0	59.0	19.0

[a] Detection limit.

major elements show values slightly higher than the typical composition of US FGD.[10]

There is absence of the potential toxic elements As, Cd, Cr, Ni, Pb and Ce, which show values below the detection limits (Table 4). Furthermore the concentrations of Cu, Mn, Mo, V and Zn are relatively low.

Mineral chemistry using microprobe analysis

The composition of the synthetic gypsum crystals (Table 5) indicates high concentrations of CaO and SO_3, the main components of gypsum. These values range from 32–46% and from 32.5–46.4%, respectively. In addition small amounts of $SiO_2 < 0.45\%$ were detected.

Table 5. Chemical composition of Florina FGD gypsum (FFGD) crystals (wt%) using microprobe analysis

Elements	Mean values	Standard deviation	Minimum values	Maximum values
SiO_2	0.39	0.04	0.34	0.43
CaO	32.31	0.25	31.99	32.51
SO_3	46.19	0.26	45.90	46.42
H_2O[a]	20.48	0.15	20.28	20.60

[a] Calculated from mineral formula $CaSO_4.2H_2O$.

Morphology of the FGD gypsum

The FGD gypsum, as shown by SEM (Fig. 3), consists of synthetic gypsum crystals with particle sizes that range from 5–50 μm, mainly rhomboidal in shape.

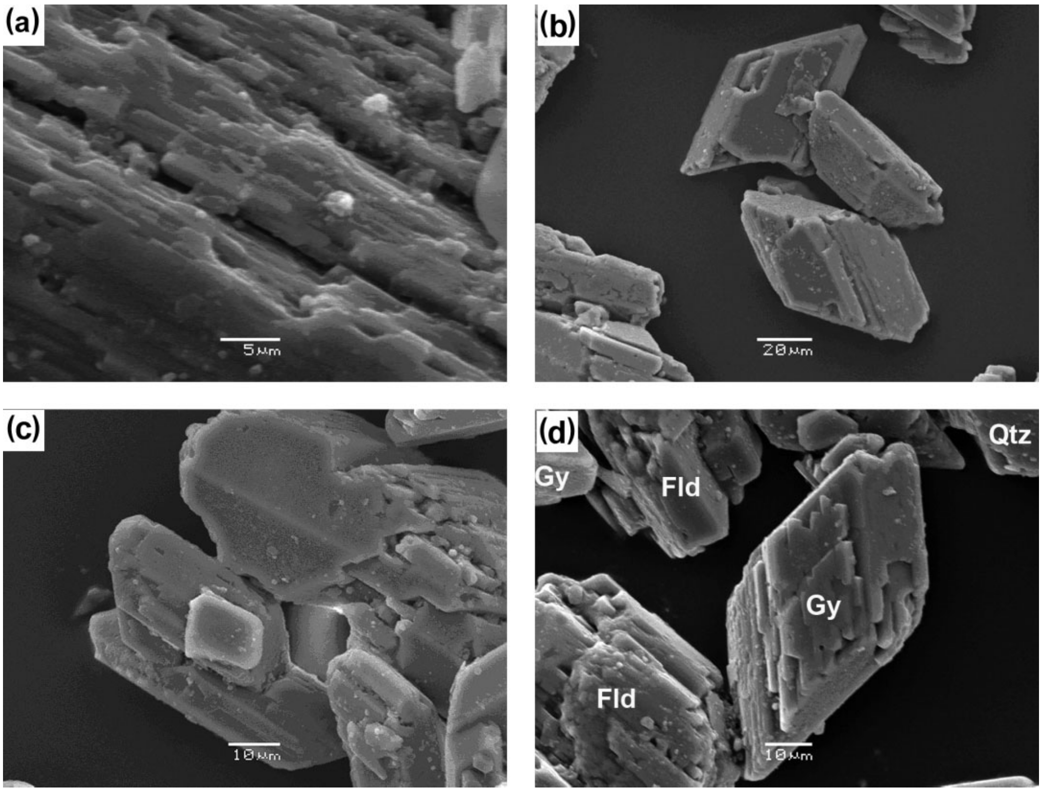

Figure 3. Scanning electron microscope images of FGD gypsum samples: (a) habit of the Florina's FGD gypsum crystals; (b) size distribution of the gypsum crystals; (c) FGD gypsum crystals, twins in the middle of the image; (d) rhomboid shape of FGD gypsum crystals (Gy) with crystals of feldspars (Fld) and quartz (Qtz).

DISCUSSION

The gypsum used in the Greek cement industry is gypsum rock extracted from quarries located in the Greek islands of Crete and Zakynthos. After quarrying, the mineral gypsum has to be crushed and transported several hundred miles for use in cement production. As those two islands are situated in the southern part of Greece and the cement industries are located in the north, the cost of gypsum is an important factor in cement production. The possibility of substituting natural gypsum with FGD gypsum, especially in the cement plants of northern Greece, such as in Thessaloniki, is considered highly important for the cement industry. The cost of transportation could be largely eliminated as the distance between Florina and Thessaloniki is only about 150 km.

Mineralogically, the natural gypsum used in the cement industry consists of monoclinic crystals with a hardness of 2. Its characteristic feature is the development of twinned crystals as a result of the formation of gypsum from the oxidation of sulphate minerals in the presence of $CaCO_3$. Natural gypsum can also be found in the form of lenses formed as a chemical sediment following evaporation and concentration of $CaSO_4$-rich waters in an alkaline environment. Quartz (SiO_2) as well as halite (NaCl) and sulphur crystals are usually identified as enclosures in natural gypsum and these impurities affect the quality and applications of the natural gypsum.

The mineralogical investigation carried out in this work showed that the Florina (Meliti) FGD gypsum is a pure material identical to mineral gypsum. XRD measurements on the FGD product show peaks identical to standard mineral gypsum. Crystals of quartz and feldspars identified by SEM scanning are of minor importance.

Florina FGD gypsum is considered comparable to other referenced FGD by-products. The by-products from dry FGD processing are mainly calcium sulphite, fly ash, portlandite [$Ca(OH)_2$] and/or calcite, as a result of the use of calcium-based sorbents, limestone or lime, in the desulphurization processes. A similar composition is reported for FGD by-products from coal fired power plants in Hong Kong, where gypsum with $CaCO_3$ and $Ca(OH)_2$ was found.[11] In other cases, hannebachite ($CaSO_3{\cdot}0.5\,H_2O$) is reported.[12–15] The by-products from the wet FGD process consist mainly of wet calcium sulphite or calcium sulphate with small amounts of fly ash, with some magnesium sulphite and magnesium sulphate, depending on the composition of the calcium-based sorbents, for example the use of dolomite.

Geochemically the natural gypsum from Crete used in cement has CaO values ranging from 32–42% and SO_3 from 44–54%. The SiO_2 content is 1–1.5%, while Al_2O_3–FeO and MgO values are 0.5–0.6% and 0.4–0.6%, respectively. In addition, NaCl content is 0.18–0.23% and CO_2 ranges from 2–2.5%. The water content of this natural gypsum has been estimated at approximately 16%.

The CaO content of the Florina (Meliti) FGD gypsum is 32%, the SO_3 content is 45–46%, while Al_2O_3

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ranges from 0.09–0.11%, Fe_2O_3 from 0.11–0.13%, MgO 0.58–0.60%, K_2O from 0.03–0.04%, and water content estimated at 20%. In comparison with natural gypsum, the FGD product has a similar composition in terms of CaO and SO_3, while the Al_2O_3 and Fe_2O_3 content is lower. This is due to the absence of clays and iron minerals present in the natural material, in the FGD gypsum.

Concerning potential toxic elements such as As, Cd, Cr, Ni, Pb and Se, chemical analysis showed that the concentrations in the Florina FGD are below the detection limit. Other trace elements, Cu, Mn, Mo, V and Zn were detected but at only low concentrations. The appearance of these trace elements in the FGD product is due to the fact that the xylitic lignite which feeds the Florina (Meliti) power station is mixed with clays, sand and silt from interbedded material in the lignite seams and contains remains of the ultramafic rocks that surround the lignite basin. Some trace elements such as V and Zn may appear in FGD gypsum from the use of limestone in the desulphurization process. However, the concentration of Cu is far below the maximum and average values reported for gypsum used for the production of cement (Table 4). Similar low values were found for vanadium, and the concentrations of Zn are within the accepted range for use in cement, but are slightly above the reported average value (Table 4).

Overall the chemical composition of the Florina FGD gypsum is similar to that reported by previous researchers in the USA[10] (Table 3).

The above results are considered promising for the potential substitution of natural gypsum by FGD gypsum in cement production. This is also confirmed by tests carried out for the production of cement with different proportions of FGD gypsum replacing natural gypsum.[17–20] The use of FGD gypsum in cement showed that the SO_3 content is within the optimum range for cement while the moisture content allows easy handling.

CONCLUSIONS

The mineralogical analysis of the FGD samples collected from the Meliti thermal power plant in north-west Greece shows that the FGD material comprises pure, fine grained, mineral gypsum with minor amounts of albite ($NaAlSiO_3$) and quartz (SiO_2).

The FGD gypsum crystals are mainly rhomboidal in shape with a particle size ranging from 5–50 μm. Microprobe analysis of the crystals shows that the concentration of CaO ranges from 31.18–34.90%, SO_3 between 42.48% and 48.40% and SiO_2 varies from 0.34–0.43%. The concentrations of TiO_2, Al_2O_3, FeO, MnO, MgO, Na_2O, K_2O and P_2O_5 are below the detection limit. The chemical composition of the major elements in Florina FGD gypsum are similar to those reported for US FGD gypsum.

Concentrations of potentially toxic elements As, Cd, Cr, Ni, Pb and Se, are below the detection limit of the ICP-AS analytical method, and the values of Cu, Mn, Mo, Cu, V, Zn, are within the limits accepted for gypsum use in cement. The origin of these trace elements is probably the xylitic lignite that is burnt in the power station containing clays, sand and silt from the interbedded material in the lignite seams. The presence of V and Zn is probably the result of using limestone in the desulphurization process.

Mineralogy and chemistry play an important role in defining the features of FGD. The main factors that affect the FGD are the composition of the coal and sorbents, conditions of the combustion, mineralogy and composition of the fly ash, and the reagent ratios.

It has been shown that the Florina FGD gypsum can substitute natural gypsum in cement production as the mineralogical and chemical data show that it is identical to the mineral, with no harmful impurities; in addition no crushing and grinding is required, and it is available in the vicinity of the cement plants.

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