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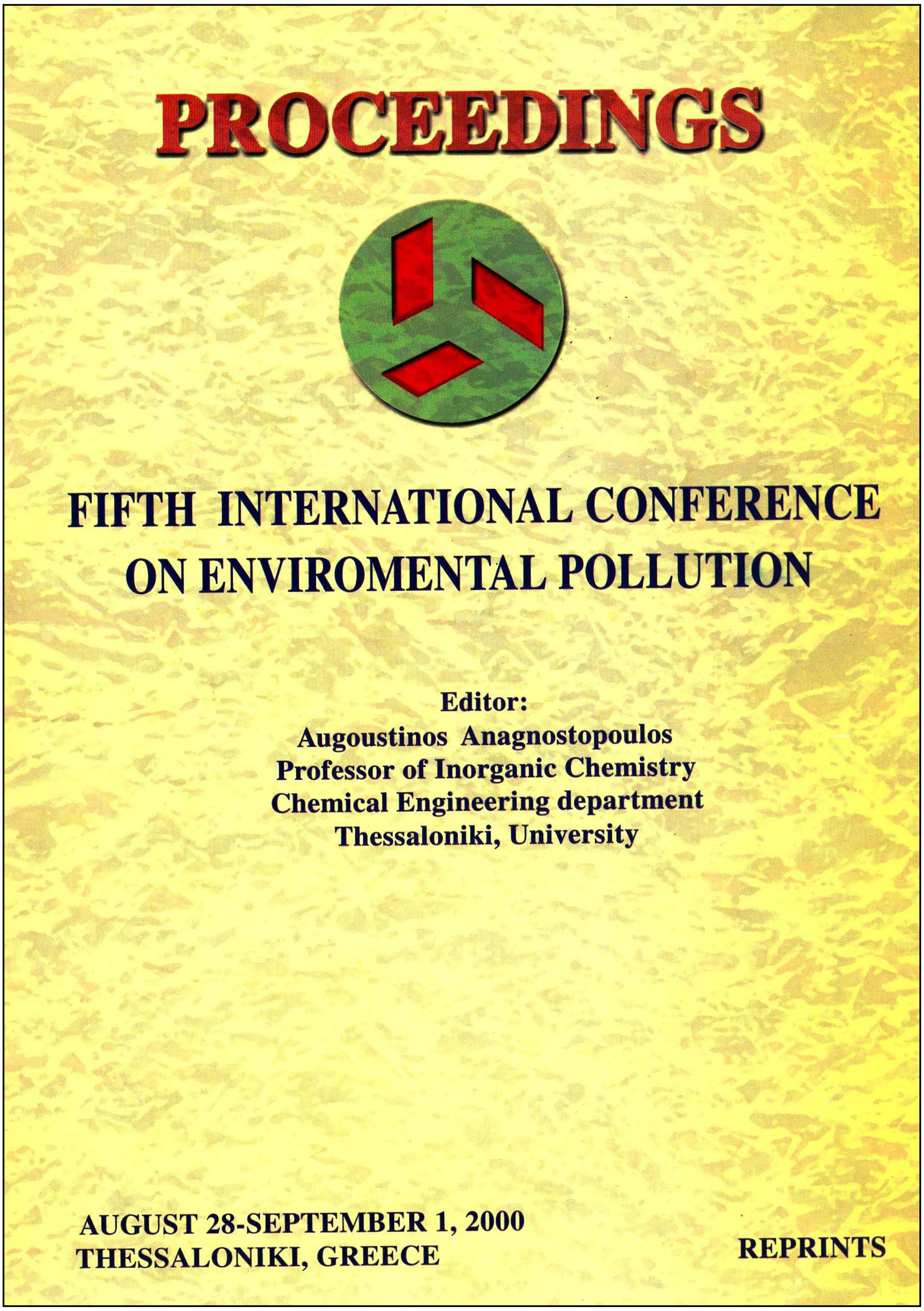

ENVIRONMENTAL USES OF LIME FROM AGIOS PANTELEIMONAS, FLORINA, MACEDONIA, GREECE

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ABSTRACT

Test specimens of the gray-green crystalline limestone from Agios Panteleimonas, Florina, were calcined at 1050°C to produce high-calcium quicklime. The average CaO+MgO content of the calcined specimens is 91.28%. In addition, their physicochemical characteristics are: available lime index 88%, $CaCO_3$ equivalent on dry basis 160%, basicity factor 0.97 and CO_2 1.75%. The studied Agios Panteleimonas lime may be used in the following environmental applications: sewage and industrial waste treatment; gaseous effluent removal; reduction of dioxins, furans and volatile heavy metals; treatment of contaminated soils; destruction of organic wastes; raise of pH of acidic ponds and lakes.

ΠΕΡΙΒΑΛΛΟΝΤΙΚΕΣ ΧΡΗΣΕΙΣ ΤΗΣ ΑΣΒΕΣΤΟΥ ΤΟΥ ΑΓΙΟΥ ΠΑΝΤΕΛΕΗΜΟΝΑ ΦΛΩΡΙΝΑΣ, ΜΑΚΕΔΟΝΙΑ, ΕΛΛΑΣ

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ΠΕΡΙΛΗΨΗ

Αντιπροσωπευτικά δείγματα του τεφροπράσινου κρυσταλλικού ασβεστόλιθου του Αγίου Παντελεήμονα Φλώρινας ασβεστοποιήθηκαν στους 1050°C για την παραγωγή υψηλού-ασβεστίου ασβέστου. Το μέσο περιεχόμενο των ασβεστοποιημένων δειγμάτων σε CaO+MgO είναι 91.28%. Επιπρόσθετα, τα φυσικοχημικά χαρακτηριστικά τους είναι: δείκτης διαθέσιμης ασβέστου 88%, ισοδύναμο $CaCO_3$ επί ξηρού 160%, συντελεστής βασικότητας 0,97 και CO_2 1,75%. Η άσβεστος του Αγίου Παντελεήμονα που μελετήθηκε μπορεί να χρησιμοποιηθεί στις ακόλουθες περιβαλλοντικές εφαρμογές: κατεργασία αποβλήτων (οικιακών και βιομηχανικών), απομάκρυνση αέριων ρυπαντών, περιορισμός διοξινών, φουρανών και πτητικών βαρέων μετάλλων, κατεργασία μολυσμένων εδαφών, καταστροφή οργανικών ρυπαντών και αύξηση του pH όξινων λιμνών.

INTRODUCTION

The term "lime" refers primarily to six chemicals produced by the calcination of high-purity calcitic or dolomitic limestone followed by hydration where necessary. They are (1) quicklime, calcium oxide (CaO); (2) hydrated lime, calcium hydroxide [$Ca(OH)_2$]; (3) dolomitic quicklime ($CaO \cdot MgO$); two types of dolomitic hydrate, (4) type N [$Ca(OH)_2 \cdot MgO$] and (5) type S [$Ca(OH)_2 \cdot Mg(OH)_2$]; and (6) dead-burned dolomite. Non dolomitic quicklime and hydrated lime are also called high-calcium lime [1].

Lime and lime products are used to adjust the pH, to clarify and to soften water. Certain sewage treatment processes use hydrated slaked lime to assist settling and compaction. Lime can also be used to disinfect sewage prior to spreading on the land. Liquid effluents are treated with hydrated lime to neutralize acidity, precipitate heavy metals and to assist settling of suspended solids. Hydrated lime can be used to remove acid gases from effluents, including sulphur dioxide. It is also used as a carrier for activated carbon/lignite coke in the removal of dioxins, furans and heavy metals from flue gases. Finally, lime can also be used to adjust the pH of agricultural land, for soil stabilisation, to raising the pH of acidic ponds and lakes, for the destruction of organic wastes and as binding agent for the briquetting of fuels [2-4].

The environmental application of lime in Europe in 1992 was 11% of the total lime market [5], while in 1984 the corresponding percentage in USA was 23% [3]. The production of lime in Greece in 1994 was 500000 tonnes, while the world total production was 118 million tonnes [4].

The average unit value of all lime sold or used by producers in 1997 was $60.70 per tonne, while the average value of high-calcium quicklime sold was $56.70 per tonne and for high-calcium hydrated lime was $75.70 per tonne [1, 3, 5].

In this paper, using the chemical composition of the materials and some of their physicochemical characteristics, we study the use of quick- and hydrated lime of Agios Panteleimonas, Florina that was produced at laboratory scale, for different environmental applications.

MATERIALS AND METHODS

Test specimens of the gray-green crystalline limestone [6] from Agios Panteleimonas region of Florina, Macedonia, were calcined at 1050°C to produce high-calcium quicklime. Preheating lasted 150 min, while the retention time at the selected temperature was 120 min. Calcination was performed in a Naber-Multitherm N11/HR furnace with accuracy ±2°C. In total, 12 specimens were calcined.

From surface and core sites of each calcined test specimen material was taken, ground and analysed by X-ray diffraction (XRD) using a Philips diffractometer with Ni-filter Cuk_α radiation. Randomly oriented samples were scanned over the interval 3-43° 2θ at a scanning speed of 1°/min in order to estimate the calcination and hydration degree of the studied test specimens. Another part of the material taken from the calcined test specimens, was homogenised and pulverised for chemical analysis by the Inductively Coupled Plasma Mass Spectroscopy (ICPMS) method.

A third part of the ground material from the calcined test specimens was hydrated as described in the standard ASTM C110/1995 [7] for physical testing of quicklime, hydrated lime and limestone in order to measure, using the standard ASTM C25/1995b [8], the available lime index, the calcium carbonate equivalent (CCE), the basicity factor (BF) and the free moisture of the produced hydrated lime. The above parameters plus CO_2 were also measured for the quicklime produced from the calcination of the initial material.

Finally, the ASTM standards C602/1995a [9] for agricultural liming materials, the C826/1994 [10] for lime and limestone products for industrial waste treatment and the C977/1995 [11] for quicklime and hydrated lime for soil stabilisation were used to examine the possible environmental applications of the studied lime.

RESULTS AND DISCUSSION

The results of the X-ray data showed that the gray-green crystalline limestone from Agios Panteleimonas was fully calcined at 1050°C. Also the hydration of the produced quicklime was completed.

The results of chemical analysis of the calcined specimens from the gray-green crystalline limestone are shown in Table 1. The average CaO+MgO content of the calcined specimens is 91.28%.

TABLE 1. Chemical analysis* (wt. %) of the calcined specimens.

SiO_2	1.09	Na_2O	<0.01
TiO_2	0.02	K_2O	<0.01
Al_2O_3	0.36	P_2O_5	<0.01
Fe_2O_3(t)	0.05	NiO	<0.01
MnO	<0.01	Cr_2O_3	<0.01
MgO	1.65	L.O.I.	7.31
CaO	89.53	Total	100.01

*Average from 12 samples.

The physicochemical characteristics necessary to be known for the environmental applications of the high-calcium quick- and hydrated lime for Agios Panteleimonas, are given in Table 2.

TABLE 2. Physicochemical characteristics* of the high-calcium quick- and hydrated lime.

	Quicklime	Hydrated lime
Available lime index (%)	88.00	77.00
Calcium Carbonate Equivalent (CCE) on dry basis (%)	159.90	125.60
Basicity Factor (BF)	0.97	0.75
Free Moisture (%)	-	1.10
CO_2 (%)	1.75	3.52

* Average from 6 samples.

Kantiranis [6] studying the gray-green limestone of Agios Panteleimonas concluded that it was a sufficient pure carbonate rock both mineralogically and chemically.

Kantiranis et al. [12] studying the volatilization of arsenic during calcination of crystalline limestone from Agios Panteleimonas found that the depletion of As in the calcined samples indicates organic affinity in the limestone and the majority of it will probably be released to the atmosphere as vapour phase.

Kantiranis et al. [13] studying the technological characteristics of the calcined limestone from Agios Panteleimonas found that the dry apparent weight of the calcined samples (1.577 g/cm^3), its low shrinkage (0.1-0.3%), the 2% impurities content and the 24% value of the attrition and abrasion resistance, characterize this quicklime and classify it to the high quality products.

Kantiranis et al. [14] studying the role of the organic matter of carbonates rocks in the reactivity of the produced lime found that the quicklime from the gray-green crystalline limestone from Agios Panteleimonas had high porosity value (~47%), neutralization equivalent OH^- ~25mol/kg and reactive CaO ~85%.

Kantiranis et al. [15] studying the high-calcium lime (quick- and hydrated) found that the requirements of the standard DIN 19611 (appearance of the aqueous solutions, neutralization equivalent OH^-, proportion by mass of Mg^{2+} and SO_4^{2-}, proportion by mass of water-soluble CaO and $Ca(OH)_2$, as well as residue remaining after dry and wet sieving) for use in water treatment, are satisfied by the pulverized high-calcium quicklime, as well as by the hydrated high-calcium lime from Agios Panteleimonas.

For sewage treatment any commercial quick- and hydrated limes are suitable [2, 4]. As reported in the standard ASTM C826/94 [10] the use of a high-calcium lime (quick- and hydrated) for industrial waste treatment must have the following chemical requirements: a) quicklime, CaO+MgO min 90.0

% and basicity factor (BF) >0.93, b) hydrated lime, CaO+MgO min 95.0 %, CO_2 max 5.0 % and BF >0.72.

The uses of high-calcium lime (quick- and hydrated) for the removing of gaseous effluents (SO_2, HCl, HF) and also for the reduction of dioxins, furans and volatile heavy metals have no chemical requirements, but they will be more effective if they have high surface area (BET) and are fine ground [2-4].

Without limits is the use of high-calcium lime (quick- and hydrated) for the treatment of contaminated land to raise the pH of soils contaminated with cadmium and other heavy metals or to disperse mineral oils and similar substances [4]. Also, high-calcium lime without requirements can be used for the destruction of organic wastes. The role of the lime is presumably to maintain the alkaline conditions favouring the hydrolysis of the organic matter and to react with inorganic oxidation products such as sulfuric acid [4]. Hydrated high-calcium lime has frequently been proposed as a binding agent for the briquetting of fuels. Its potential for binding some of the sulfur in the fuel and the application without requirements made it a particularly attractive agent [4].

High-calcium quicklime with MgO <5% and hydrated lime without limitations are used in agriculture (soil treatment) [4]. Boynton [2] reports that high-calcium quicklime must have an available lime content at least 85% for use in agriculture, while the corresponding value for hydrated lime must by et least 70%. For the same use in the standard ASTM 602/1995a [9] it is reported that the calcium carbonate equivalent (CCE) for high-calcium quicklime must be at least 140 %, while for hydrated lime must be at least 110 %. Also, high-calcium lime can be used for soil stabilization. As reported in the standard ASTM 977/1995 [11] quicklime and hydrated lime shall conform to the following chemical composition: CaO+MgO (on a LOI-basis, min %) 90.0, CO_2 (max %) 5.0 and free moisture (max, %) 2.0. The last use of lime that studied in this case is concerned hydrated high-calcium lime for raising the pH of acidic ponds and lakes. Also this use is without any requirements [4].

CONCLUSIONS

Based on the chemical analyses of the calcined specimens and the physicochemical characteristics of the produced high-calcium quick- and hydrated lime, the following environmental uses can be proposed for the Agios Panteleimonas lime:

- For sewage and industrial wastes treatment.
- To remove gaseous effluents as SO_2, HCl and HF. Also for the reduction of dioxins, furans and volatile heavy metals. Also can be used for the destruction of organic wastes.
- The hydrated high-calcium form can be used as a binding agent for the

briquetting of fuels.

- Both types, high-calcium quick- and hydrated lime can be used in agriculture mainly for soil treatment (i.e., raise the pH or treat the contaminated soil). Also, both types of lime can be used for soil stabilization.
- The hydrated high-calcium lime can be used to raise the pH of acidic ponds and lakes.

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