Investigation of carbonate rocks appropriate for the production of natural hydraulic lime binders

CONFERENCE PAPER · APRIL 2014

READS
32

5 AUTHORS, INCLUDING:

George Triantafyllou
Technical University of Crete
21 PUBLICATIONS **3** CITATIONS
SEE PROFILE

George Panagopoulos
Technical University of Crete
17 PUBLICATIONS **6** CITATIONS
SEE PROFILE

Emmanouil Manoutsoglou
Technical University of Crete
89 PUBLICATIONS **162** CITATIONS
SEE PROFILE

G.E. Christidis
Technical University of Crete
48 PUBLICATIONS **690** CITATIONS
SEE PROFILE

Geophysical Research Abstracts
Vol. 16, EGU2014-7890, 2014
EGU General Assembly 2014

Investigation of carbonate rocks appropriate for the production of natural hydraulic lime binders

George Triantafyllou (1), George Panagopoulos (1), Emmanouil Manoutsoglou (1), George Christidis (1), and Richard Přikryl (2)

(1) Technical University of Crete, School of Mineral Resources Engineering, Chania, Greece (gtriant@mred.tuc.gr, +00302821069554), (2) Charles University in Prague, Faculty of Science, Institute of Geochemistry, Mineralogy and Mineral Resources, Albertov 6, 128 43 Prague 2, Chech Republic (prikryl@natur.cuni.cz)

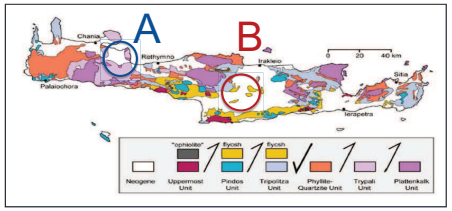
Cement industry is facing growing challenges in conserving materials and conforming to the demanding environmental standards. Therefore, there is great interest in the development, investigation and use of binders alternatives to Portland cement. Natural hydraulic lime (NHL) binders have become nowadays materials with high added value, due to their advantages in various construction applications. Some of them include compatibility, suitability, workability and the versatility in applications. NHL binders are made from limestones which contain sufficient argillaceous or siliceous components fired at relatively low temperatures, with reduction to powder by slaking with or without grinding. This study is focused in developing technology for small-scale production of cementitious binders, combining the knowledge and experience of geologists and mineral resources engineers. The first step of investigation includes field techniques to the study the lithology, texture and sedimentary structure of Neogene carbonate sediments, from various basins of Crete Island, Greece and the construction of 3D geological models, in order to determine the deposits of each different geological formation. Sampling of appropriate quantity of raw materials is crucial for the investigation. Petrographic studies on the basis of the study of grain type, grain size, types of porosity and depositional texture, are necessary to classify effectively industrial mineral raw materials for this kind of application. Laboratory tests should also include the study of mineralogical and chemical composition of the bulk raw materials, as well as the content of insoluble limestone impurities, thus determining the amount of active clay and silica components required to produce binders of different degree of hydraulicity. Firing of the samples in various temperatures and time conditions, followed by X-ray diffraction analysis and slaking rate tests of the produced binders, is essential to insure the beneficiation of their behavior. Beneficiation is defined as the implementation of the best available techniques to insure the production of an economically usable final product which combines both the hydraulicity of the silicates, aluminates and ferrites, as well as the reactivity of the calcium oxide amounts that are present.

Investigation of carbonate rocks appropriate for the production of natural hydraulic lime binders

George Triantafyllou (1), George Panagopoulos (1), Emmanouil Manoutsoglou (1), George Christidis (1) and Richard Přikryl (2)
(1) Technical University of Crete, Mineral Resources Engineering Department, Chania, 73 100, Greece (gtriant@mred.tuc.gr),
(2) Charles University in Prague, Faculty of Science, Institute of Geochemistry, Mineralogy and Mineral Resources, Albertov 6, 128 43 Prague 2, Czech Republic (richard.prikryl@natur.cuni.cz)

Introduction

Cement industry is facing growing challenges in conserving materials and conforming to the demanding environmental standards. Therefore, there is great interest in the development, investigation and use of binders alternatives to Portland cement. Natural hydraulic lime (NHL) binders have become nowadays materials with high added value, due to their advantages in various construction applications. Some of them include compatibility, suitability, workability and the versatility in applications. NHL binders are made from limestones which contain sufficient argillaceous or siliceous components fired at relatively low temperatures, with reduction to powder by slaking with or without grinding. This study is focused in developing technology for small-scale production of cementitious binders, combining the knowledge and experience of geologists and mineral resources engineers.

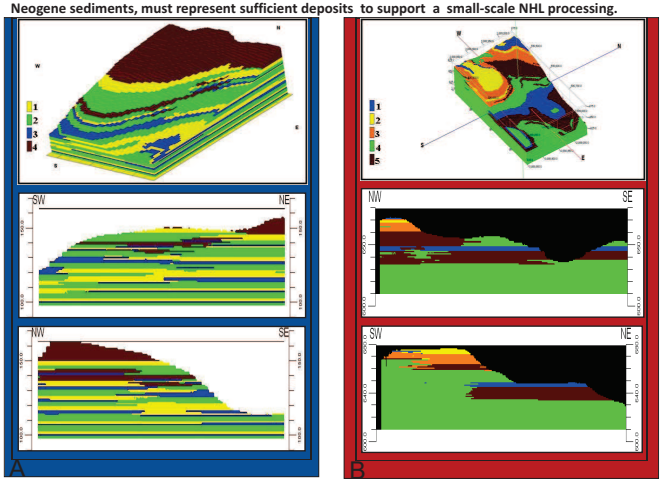


Simplified geologic map of the basement units of Crete and their tectonostratigraphic relationships. Sampling areas from Neogene basins are pointed in circles.

Several Neogene carbonate sediments were collected and investigated, as potential geomaterials for the production of NHL binders. Geochemistry and mineralogy of both the bulk samples and their insoluble residue, are used to characterize the sediments and to determine the amount of active clay and silica components required to produce after firing, binders of different degree of hydraulicity. Feature results of this study are presented herein.

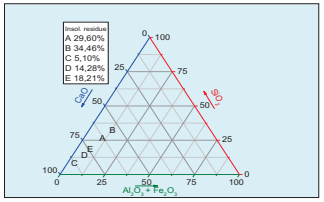
Field Techniques – 3D Neogene lithotype models

3D geological models are used to comprehend complex geological structures and to carry out volume calculations. Carbonate rocks classified after petrographic studies, mineralogy and chemistry as various Neogene sediments, must represent sufficient deposits to support a small-scale NHL processing.

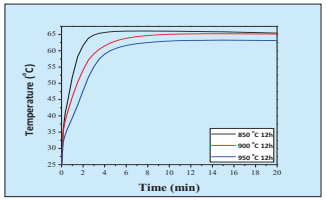


3D geological models and the corresponding geological sections obtained from topographical and geological field data, using the RockWorks software. Captions: A) Apokoronas basin, 1. non laminated calcareous marls (Sample A), 2. laminated calcareous marls (Sample B), 3) bioclastic limestones and 4) marly limestones. B) Agia Varvara basin, 1. reefal limestones, 2. calcareous marls (Sample E), 3. marly limestones (Samples C & D), 4.sandstones, 5. sandy limestones. All studied samples are of Upper Miocene (Messinian) age / Vrysses Formation.

Experimental Results

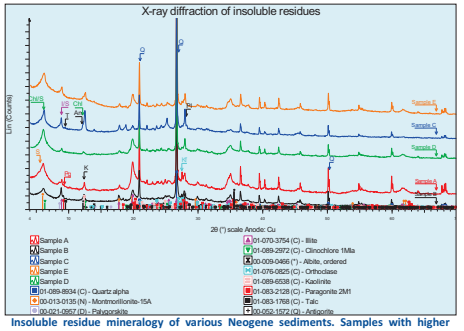


The quality of raw materials is directly related to the chemistry and homogeneity of carbonate rocks , the amount and quality of the insoluble residue, which in turn depend on the lithology of the formations.



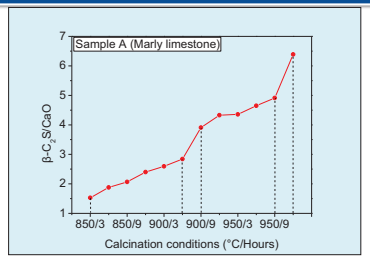
Laboratory slaking rate tests were performed for each product, indicating the optimum conditions in order to obtain high reactive hydraulic lime binders.

Experimental Results

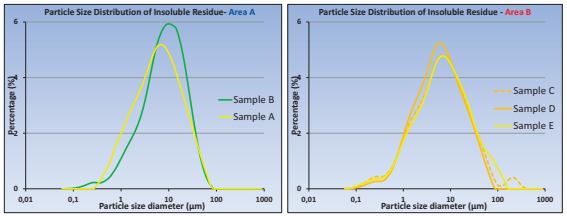


Insoluble residue mineralogy of various Neogene sediments. Samples with higher amounts of ins. residue (mainly marly limestones and calcareous marls), thus richer in clay minerals (illite, kaolinite, montmorillonite, paragonite) give after firing NHL binders with higher proportions of calcium aluminates and calcium aluminosilicates comparative to other raw materials.

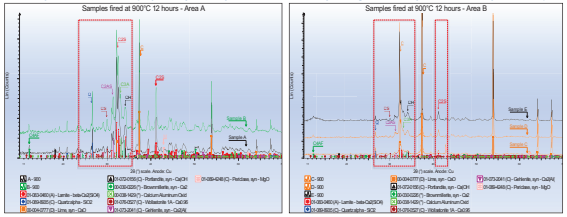
Firing experiments – Various NHL products



Firing of the samples in various temperatures and time conditions, followed by quantitative X-ray diffraction analysis, showed the production of binders of different degree of hydraulicity from the same raw material. The variance ratio of β-C_2S/CaO, indicates three different fields of firing which decisively affect the mineralogical composition and thus the characteristics of produced cement. Up to 900°C and 6 hours the products are moderately natural hydraulic limes, after until 950°C and 9 hours eminently NHL and the product at 950°C and 12 hours considers to be a Natural Cement binder. Calcination conditions and not only the lithotype of the raw material are those which largely determine the type of cementitious binders produced.



Particle size analysis of the insoluble residue by laser diffraction. The grain-size distribution functions of unimodal or polymodal residues, significantly affect the firing process in each sample and the mineralogy of the produced binders (especially in the presence of coarse quartz grains, comparison of samples C & D).



X-ray diffraction patterns of hydraulic limes produced after calcination. The binders contain different amounts of cement phases (calcium silicates, calcium aluminates, calcium aluminosilicates and ferrites), lime/portlandite and unreacted silica and display various hydraulicity. C_2S-larnite, C_3A-tricalcium aluminate, C_4AF-brownmillerite, C_2AS-gehlenite, CS-wollastonite, C-calcium oxide, CH-portlandite, Q-quartz.

Conclusions

The implementation of the best available techniques, combining both field techniques and detailed laboratory analyzes are necessary to insure the production of and economically usable final product which combines both the hydraulicity of the silicates, aluminates and ferrites, as well as the reactivity of the calcium oxide amounts that are present. 3D lithostratigraphic models in combination with the appropriate experimental analyzes of selected Neogene sediments, could assist in the beneficiation of the production process of Natural Hydraulic lime binders in small-scale production plants.

References

1. Panagopoulos, G., Pyliotis, I., Zelilidis, A., Spyridonos, E., Hamdan, H., Vafidis, A. & Manoutsoglou, E., (2011). *3D modeling of biogenic gas-bearing Neogene deposits at Arkalochori region, Messara, Crete, Greece*. Proceedings of IAMG Congress, 5 – 9 September, Salzburg, pp. 431-440. doi:10.5242/iamg.2011.0281
2. Triantafyllou, G., Přikryl, R. & Markopoulos Th., (2011). *Reactivity of hydraulic binders: A proposed laboratory testing technique*. Geophysical Research Abstracts, Vol. 13, EGU2011-7424-4, Vienna.
3. Triantafyllou, G., Markopoulos, Th. & Přikryl, R., (2010). *On the mineralogy of β-dicalcium silicate of hydraulic binders in various calcination conditions*. Acta Mineralogica-Petrographica Abstract series Vol. 6, p. 133. 20th General Meeting of the IMA, Budapest, Hungary.