TECHNICKÝ A SKÚŠOBNÝ ÚSTAV STAVEBNÝ
BUILDING TESTING AND RESEARCH INSTITUTE

NOVACEM

Increasing environmental protection by innovative advanced technologies of cement production of new generation

SINTEF

CEMENTÁREŇ LADCE

GOVERNMENT OFFICE OF THE SLOVAK REPUBLIC

ICELAND LIECHTENSTEIN NORWAY eea grants

norway grants

„Supported by a grant from EEA and Norway Grants“.

Short articles based on the presentations provided on the NOVACEM workshop in Chorvátsky Grob and Ladce on 5-6 May 2015

Editor

Building Testing and Research Institute
Technický a skúšobný ústav stavebný, n.o.
Studená 3, 821 04 Bratislava
Slovakia/Slovensko
2015

Number of copies: 50

ISBN 978-80-971912-2-1

CONTENT

FOREWORD

NOVACEM project immerged due to support of "Bilateral Fund at National Level for 2014". Strategic aim of this program was development of active cooperation between Slovak and Norwegian partners within the EEA and Norway Grants. Bilateral Fund for 2014 contributes to expansion of common knowledge and mutual exchange of experience in the field of new generation cements in both countries.

The aim of NOVACEM project was the optimal development of new generation of low-energy cement based on new raw material for firing cement - marl and special cements for advanced technologies mainly for ready - mixed concrete with enhanced durability to aggressive environmental loads, so that later the solutions can be applied in practice and capitalized in high - quality joint research.

Based on existing knowledge the aim of new joint research project will be implanting new generation cements into ordinary concrete manufacturing by means of research findings oriented to the application of new generation cements in construction industry.

Universal contribution of the project was mutual knowledge transfer among scientific communities in Bratislava and Trondheim, which later should extend among people of cement production and building industry within further regions of both countries. Broad social benefit means establishing friendly contacts between scientific parties of Slovakia and Norway resulted in the common will to continue to work together.

Clays and clay minerals

Peter Komadel, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia, peter.komadel@savba.sk

Abstract

Natural or modified clays and clay minerals are abundant and inexpensive materials of this century with relatively simple fundamental structure, very attractive properties and complex industrial and environmental applications. This short communication covers only very limited summary of collected knowledge on these materials and just one type of their chemical modification.

1 Introduction

Wikipedia: says that clays are fine-grained natural rock or soil materials that combine one or more clay minerals with traces of metal oxides and organic matter. Clays are plastic due to their water content and become hard, brittle and non–plastic upon drying or firing. Different clays and clay minerals have been known and used for thousands of years for different purposes; though most of current uses of bentonites were developed after 1900. Today it is a key raw material in the production of energy and steel, and in numerous other common products and applications. This is why fine fractions of bentonites are the main materials discussed in this short communication. Several prominent contributions to clay literature have appeared very recently, including the Elements issues on bentonites (*Elements* 5(2) 2009, ed. D. C. Bain) and on kaolins (*Elements* 10(3) 2014, eds. P. A. Schroeder and D. L. Bish). The most recent and complex writing on clays is the Handbook of Clay Science edited by F. Bergaya and G. Lagaly, with Part A – Fundamentals and Part B – Techniques and Applications. In industrial applications of clays, one distinguishes four types of clays: (1) bentonites with montmorillonite as the principal clay mineral constituent; (2) kaolins containing kaolinite; (3) palygorskite and sepiolite; and (4) 'common clays', which often contain illite–smectite mixed-layer minerals, and are largely used for ceramics[1]. Bentonite is a key raw material in the production of energy and steel, and in numerous other applications that are critical to the world economy[2,3] and environment[4]. One of the most common chemical modifications of clay minerals, used for both industrial and scientific purposes, is their acid activation. This consists of the reaction of clay minerals with a mineral acid solution, usually HCl or H_2SO_4 to obtain partly dissolved material of increased surface area, porosity and surface acidity. The term acid-activated clay was reserved for partly dissolved bentonites[5].

2 Materials and Methods

Typical materials used for acid activation laboratory experiments are fine fractions of bentonites and the methods being employed to characterize the acid-activated silicates include chemical analysis of liquid and/or solid reaction products; X-ray diffraction; Mössbauer, Fourier transform infrared, and magic angle spinning nuclear magnetic resonance spectroscopies; scanning and/or transmission electron microscopies; and acidity, surface area, and pore-size measurements.

3 Results and Discussion

Upon acid treatment, protons penetrate into the mineral layers and attack the structural OH groups. The first step during acid treatment is that the protons replace the exchangeable cations; then they attack the layers. The exchange reaction is fast if there is good contact between the interlayers and the acid. The resulting dehydroxylation is connected with the successive release of the central atoms from the octahedra as well as with the removal of Al from the tetrahedral sheets. Simultaneously, a gradual transformation of the tetrahedral sheets into a three-dimensional framework proceeds. Depending on the extent of acid activation, the resulting solid product contains unaltered layers and amorphous silica, while the ambient acid solution contains ions according to the chemical composition of the clay mineral and the acid used. The final reaction product of various acid-treated clay minerals was always the same. The acid and smectite and the quantity of available protons was sufficient. The substitution rate was independent of the smectite if the clay mineral contained only swelling layers. In contrast to smectites saturated with metal cations, proton-saturated smectites were unstable. The layers were attacked by surface and interlayer hydrated protons, even after drying the separated activated smectite, similar to what occurred in solution. This process, known as 'auto-transformation', spontaneously changed H-smectites to their Al^{3+}, Fe^{3+}, or Mg^{2+}-forms on ageing in aqueous dispersion at 90 °C. Auto-transformation of the H-smectites also decreased the mean layer charge. The number of strong acid sites decreased and the number of weak acid sites increased on ageing[5] and citations therein.

4 Conclusions

Clays and clay minerals cannot be avoided from research and industry, they are essential for our existence. Acid activation of clays and clay minerals has been used for decades both in laboratories for basic and applied research and in industrial production for many applications. Even so, it remains one of the most common chemical modifications of clays and clay minerals also for the future of clay science and industry.

References

1) Bergaya F. and Lagaly G. (2013): Developments in Clay Science – Volume 5A. *Handbook of Clay Science.* A. Fundamentals. B. Techniques and Applications. Second edition, Oxford, Elsevier.
2) Eisenhour D. D. and Brown R. K. (2009) Bentonite and its impact on modern life. *Elements* **5,** (2) 83–88 (2009)
3) Guven N. (2009) Bentonites – clays for molecular engineering. *Elements* **5,** (2) 89-92.
4) Gates W. P., Bouazza A, and Churchman G. J. (2009) Bentonite clay keeps pollutants at bay. *Elements* **5,** (2) 105-110.
5) Komadel P. and Madejová J. (2013) *Acid activation of clay minerals.* Chapter 10.1, pp. 385-410 in: F. Bergaya and G. Lagaly (editors): Developments in Clay Science – Volume 5A. *Handbook of Clay Science.* A. Fundamentals. Second edition, Oxford, Elsevier.

Acknowledgement

"Supported by a grant from EEA and Norway Grants and the Research & Development Operational Programme funded by the ERDF (project No.: ITMS 26240220078)."

Various benefits of IR spectroscopy in clay minerals studies

Jana Madejová, Institute of Inorganic Chemistry, Slovak Academy of Sciences,
Dúbravská cesta 9, 845 36 Bratislava, Slovakia, jana.madejova@savba.sk

Abstract

The potential of the infrared (IR) spectroscopy in clay minerals studies is introduced. The selection of sampling techniques (transmission or reflection) for IR analysis depends on the purpose of the study and on the physical state of the sample. The KBr pressed disk technique, the most frequently used transmission method in the middle IR (MIR) region, is very useful for routine characterization of clays and to derive information concerning their composition, structure of clay minerals and changes upon their chemical modification. Diffuse reflectance (DRIFT) technique is the main method employed in the near IR (NIR) region allowing obtaining spectra of the neat samples, which simplifies and accelerates the IR measurements.

1 Introduction

IR spectroscopy has been frequently used to investigate the structure, bonding and chemical properties of clay minerals. Since the introduction of the Fourier transform (FT) instrumentation the application of the IR spectroscopy greatly increased in many spheres of clay research due to intense development of new sample-handling accessories. In addition to the traditional transmission methods (e.g. KBr pellet), the reflectance techniques such as DRIFT or attenuated total reflectance (ATR), requiring little or no sample preparation, are utilized increasingly worldwide. The purpose of this paper is not only to present various IR techniques, but also to show that the key to successful analysis is choosing the right accessory for the particular application.

2 Materials and methods

Clay minerals representing different structural groups of layer silicates were analyzed. The samples were obtained either from the Source Clay Repository of the Clay Minerals Society or from clay deposits in Slovakia. Acid treatment of clay minerals was performed in 6M HCl at different time. The organo-clays were prepared by cation exchange reaction from original clay sample and alkylammonium salt.

The IR spectra were obtained on a Nicolet 6700 FTIR spectrometer from Thermo Scientific. The KBr pressed disk technique (1 mg of sample and 200 mg KBr) and ATR accessory MIRacle^{TM} from PIKE technologies were used to measure spectra in the MIR region. NIR spectra were collected by Smart DRIFT and UpDRIFT accessory from Thermo Scientific.

3 Results and discussion

In the studies of clay minerals the absorption bands due to structural OH and Si-O groups play an important role in the differentiation of clay minerals from each other. The sensitivity of the OH stretching vibrations to structural features of the individual clay minerals permits to differentiate 1:1 *vs*. 2:1 silicate layer type and to recognize the type (di- or tri-octahedral) and chemical composition of the octahedral sheets. Structural modification of the minerals from smectite group (e.g. montmorillonite) during acid treatments was studied using KBr (MIR) and DRIFT (NIR) techniques. Protons attack the structural OH groups which results in successive release of Al and Mg atoms from the octahedral sheets. At the same time a gradual transformation of the layered tetrahedral Si-O sheet to a three-dimensional framework proceeds. The final reaction product is an amorphous partly protonated silica phase (Fig. 1).

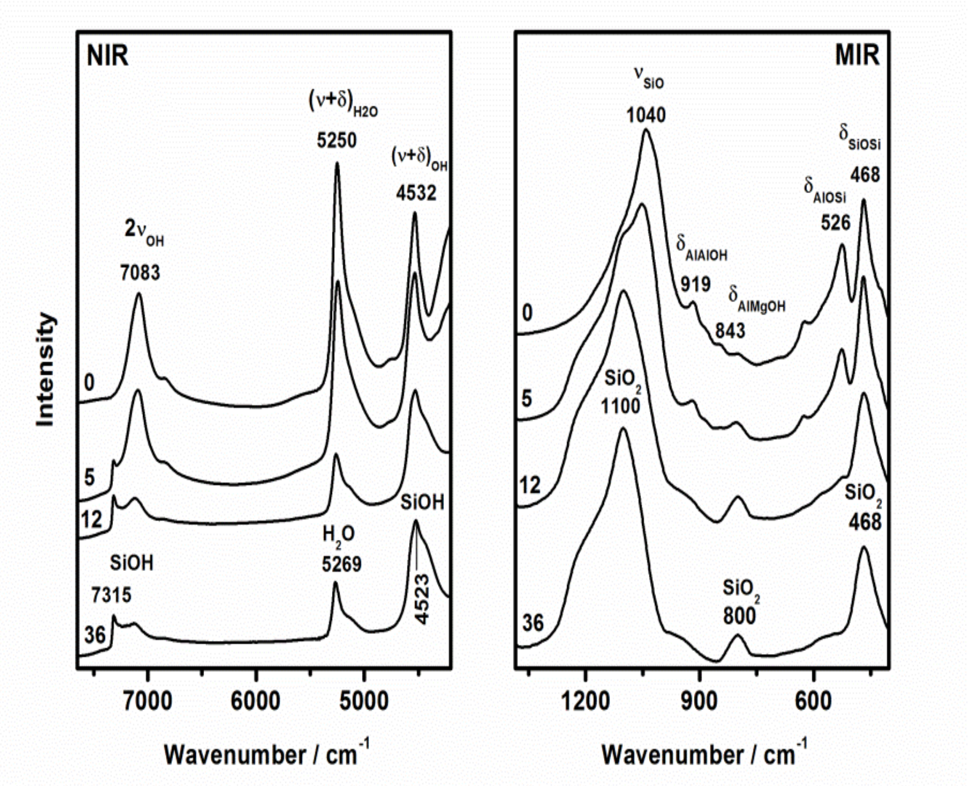


Figure 1 NIR and MIR spectra of untreated and acid treated montmorillonite Kopernica. Time of HCl treatment (in h) is indicated in the figure.

The ATR (MIR) and UpDRIFT (NIR) accessories were applied to obtain information on hydration properties of montmorillonites saturated with different exchangeable cations. Good correlation of the results obtained by IR spectroscopy and gravimetry indicated that the position and the area of absorption bands of water reasonably reflects the hydration process of montmorillonites and can be used for estimation of water content.

The IR spectroscopy is often used to characterize organically modified clay minerals. Very sensitive are NIR spectra able to identify selected functional groups (e.g. NH_2^+, NH^+, or vinyl groups) which are difficult to recognize in the MIR region due to overlapping with other absorption bands.

Acknowledgement

“Supported by a grant from EEA and Norway Grants and the Research & Development Operational Programme funded by the ERDF (project No.: ITMS 26240220078).“

Calcined marl as supplementary cementitious material (SCM)

Tone Østnor
SINTEF Building and Infrastructure, Trondheim, Norway, tone.ostnor@sintef.no

Abstract

Calcined clay or marl was rated the most promising alternative pozzolan for the future in a state of the art report[1] within COIN (COncrete INnovation Centre). Calcined marl has been proven to perform well with excellent strength at both 1 and 28 days relative to reference, when up to 50 vol. % of cement were replaced by calcined marl. A more puzzling feature is that strength continues to increase in spite of no calcium hydroxide (CH) in the system up to 2 years

1 Introduction

The objective in the COIN project was to develop an alternative pozzolan that could partly replace cement in concrete. During cement production large amounts of CO_2 are emitted. This makes it interesting to look into alternative materials instead of clinker/cement from an environmental point of view. Nowadays clinker in blended cement, or cement in concrete, is often replaced by slag or fly ash, but these supplies could become limited in the future. The state of the art report written in 2007[1] looked into different alternative pozzolans. Calcined marl was chosen because the material is fast reactive, relative low-priced, has low calcining temperature, not so well known and it is available in large quantities around the world.

2 Results and discussion

2.1 Materials

Calcining marl at 800 °C[1] in a rotary kiln will leave most of the calcium carbonate intact as shown by thermogravimetry[2, 3] and render the calcined clay pozzolanic when partly replacing Portland cement. The calcined marl was ground to D_{50} = 7 µm. Normal Portland cement (CEM I 42.5R according to NS-EN 197-1), aggregate 0 – 8 mm, Dynamon SP 130 superplasticizer was used for all the mortar mixes. The mortars were made with 0, 20, 35, 50 and 65 % volume replacement of cement by calcined marl to secure a constant volume of binder, at the same time as constant water content and equal flow was maintained by the use of plasticizers.

2.2 Compressive and flexural strength

The compressive and flexural strength were measured on the 40x40x160 mm prisms at 1, 3, 7, 28, 90 days, 1 and 2 year of curing according to NS-EN 196-1. The development of the compressive strength for all mortars as a function of time is given in Figure 1.

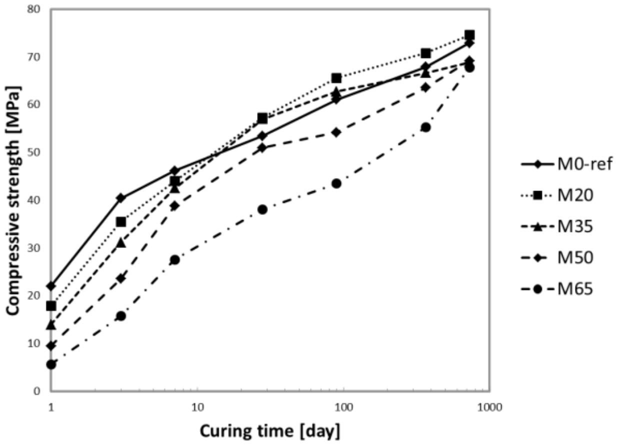


Figure 1 Compressive strength development of mortar mixes where cement is replaced with 0 (M0), 20 (M20), 35 (M35), 50 (M50) and 65 (M65) vol. % calcined marl.

There are three hypotheses that might explain the strength increase after all CH is depleted[4]:

1) There are two types of CSH in the system. One with high C/S from hydration of cement and one with low C/S from the direct pozzolanic reaction between calcined marl and calcium hydroxide. The one with higher C/S has higher solubility of Ca^{2+} and is considered weaker mechanically than the one with lower C/S. Slowly the two different CSHs will equilibrate to an overall stronger CSH with intermediate C/S.
2) The solubility of Ca^{2+} from CSH with high C/S and pH is so high that one can have a direct further pozzolanic reaction with unreacted calcined marl.
3) The silicate anions of in particular CSH with low C/S will polymerize over time creating longer chain lengths of the CSH which may lead to even higher strength.

3 Conclusions

Calcined marl - ordinary "blue" clay containing calcium carbonate – can be an effective pozzolan in cementitious materials if calcined at the correct temperature. Marl is unsuitable for the clay product industry, and might thus be the high-volume alternative pozzolan available globally that the cement and concrete industry is looking for in order to reduce their carbon footprint.

Excellent strength at both 1 and 28 days relative to reference is obtained when up to 50 vol. % is replaced by calcined marl. Strength continues to increase to 2 year in spite of no CH.

References

1) Østnor, T., "Alternative pozzolans as supplementary cementitious materials in concrete" State of the art report, COIN 2007. www.coinweb.no
2) Justnes, H., Østnor, T. and Danner, T.: "Calcined Marl as Effective Pozzolana", Proc. Int. RILEM Conference on Advances in Construction Materials Through Science and Engineering, RILEM PRO 79, 5-7 September, 2011, Hong Kong, China, 8 pp.
3) Danner, T. "Reactivity of Calcined Clays", Doctoral Thesis at NTNU, 2013:218, 223 pp.
4) Justnes, H. and Østnor, T.: "Durability and microstructure of mortar with calcined marl as supplementary cementing material", Proc. XIII conference on Durability of Building Materials and Components (DBMC), Sao Paulo, Brazil, September 3-5, 2014, pp. 771-780

Acknowledgement

“Supported by grant from EEA and Norway Grants. The research was performed during the Concrete Innovation (COIN) programme, see www.coinweb.no.”

Recipes of mortars with calcined marl

- Industrial produced calcined marl
- 0, 20, 35, 50 and 65% replacement of cement by volume
- Ordinary Portland Cement (OPC)
- Super plasticizer ~ 0.1 – 0.8 % of binder weight
- w/b ratio 0.5 with a flow of ± 5% within the reference

- Mortar bars 40x40x160mm and cylinders 100x200 mm. Stored at 20°C and 90% RH

Microstructure and durability of mortar with calcined marl as supplementary cementitious material (SCM)

Harald Justnes
SINTEF Building and Infrastructure, Trondheim, Norway, harald.justnes@sintef.no

Abstract

Mortars (sand : cement = 3:1 and w/c = 0.50) were made where Portland cement was replaced with 0, 20, 35, 50 and 65 vol. % calcined marl. The compressive and flexural strengths were determined after 1, 3, 7, 28, 90, 365 and 730 days curing at 90 % RH and 23°C. Mortars of all compositions were tested for durability starting after 90 days curing with respect to chloride diffusion, expansion caused by sulphate attack (5 % Na_2SO_4) at both +5°C and +20°C, as well as carbonation (accelerated by 1 % CO_2 and 60 % RH). The microstructure of the mortars was characterized by SEM after 90 days and 2 years curing, as well as capillary suction and saturation giving total volume of capillary pores and amount of macro pores. Electrical resistivity was also measured.

1 Introduction

Marl, or calcareous clay, is considered ”bad” clay for production of burnt clay products (e.g. bricks and light weight aggregate) since it is clay containing substantial amounts of calcium carbonate that will form CaO after burning. This can lead to “pop outs” when calcium oxide reacts with water to calcium hydroxide during service.

Calcined marl has been proven earlier by Justnes et al[1] to be an effective pozzolan in cementitious products. Thus, marl can be a large SCM resource that is not yet exploited to make blended cements or as mortar/concrete additive. Marl with 10-20 % $CaCO_3$, or rather calcareous mudstone, was calcined at 800 °C leaving 20 % of the original $CaCO_3$ intact.

2 Results and discussion

2.1 Microstructure

The marl used consisted basically of the clay mineral smectite and 20 % calcium carbonate. About 90 % of the dominating divalent iron oxidized to trivalent leading to inclusion of one extra oxide ion (O^{2-}) in the clay lattice in addition to dehydration and collapse of the structure changing most of the octahedral coordinated aluminum to tetrahedral coordinated[2]. The amount of $CaCO_3$ surviving calcination is about 4 % of calcined clay. The products from the pozzolanic reaction of calcined marl with calcium hydroxide from cement hydration will then be more CSH and calcium aluminum hydrates (CAH) of various kinds, as well as calcium hemi- and mono-carboaluminate hydrate[3] leading to extra water binding.

2.2 Durability

Chloride ingress profiles in mortars where different portions of cement are replaced with calcined marl are shown in Fig. 1a, while the evolution of electrical resistivity for the same mortars are depicted in Fig. 1b as examples. Other durability data is available from Justnes and Østnor[3] showing that carbonation resistance is decreasing with increasing cement replacement as for most blended cements and that the resistance to sulphate attack is improved. The total capillary porosity increases when crystalline CH is transformed to CSH in the pozzolanic reaction, but pore sizes are probably refined and partly segmented.

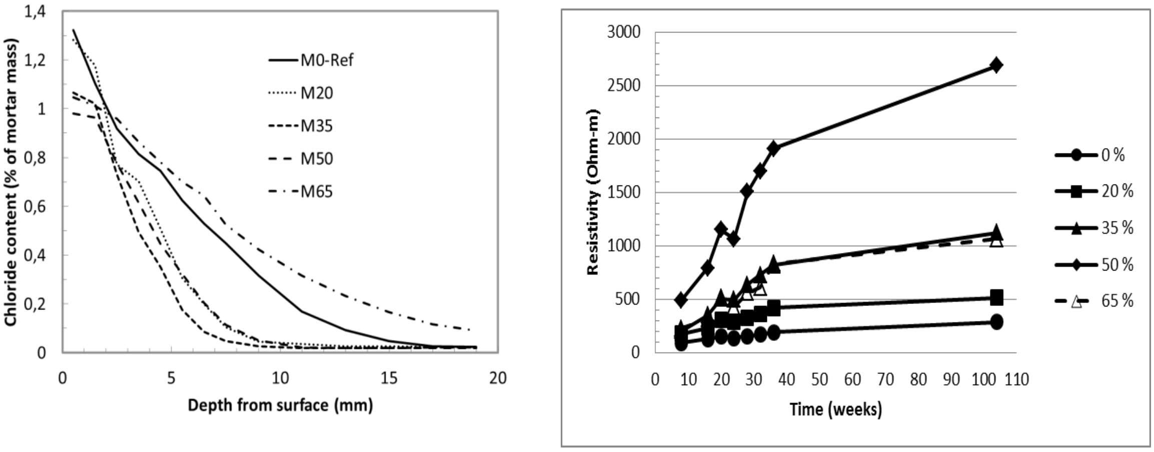


Figure 1a: Chloride ingress in mortars where cement is replaced with 0 (M0), 20 (M20), 35 (M35), 50 (M50) and 65 (M65) vol. % calcined marl after 35 days to 165 g NaCl/liter. 1b: Electrical resistivity as function of time for the same mortars cured in water at 20 °C.

3 Conclusions

Excellent strength at both 1 and 28 days relative to reference is obtained when up to 50 vol. % is replaced by calcined marl. Pozzolanic products from marl are more CSH and different CAH including calcium carboaluminate hydrates. The capillary porosity volume is increasing, but the electrical resistivity is also increasing, indicating a pore refinement or segmentation, as well as perhaps reduced ionic strength in the pore water. These are properties that might reduce the propagation rate of rebar corrosion once initiated. The chloride ingress is drastically reduced relative to reference for mortars with ≤ 50 % marl replacing cement, but the accelerated carbonation rate is increasing (as for all blended cements at equal w/c.) The reduced carbonation resistance may be less in practice with much lower CO_2 concentration and carbonation happening over years while the pore structure continuously densifies.

References

1) Justnes, H., Østnor, T. and Danner, T.: "Calcined Marl as Effective Pozzolana", Proc. Int. RILEM Conference on Advances in Construction Materials Through Science and Engineering, RILEM PRO 79, 5-7 September, 2011, Hong Kong, China, 8 pp.
2) Danner, T. "Reactivity of Calcined Clays", Doctoral Thesis at NTNU, 2013:218, 223 pp.
3) Justnes, H. and Østnor, T.: "Durability and microstructure of mortar with calcined marl as supplementary cementing material", Proc. XIII conference on Durability of Building Materials and Components (DBMC), Sao Paulo, Brazil, September 3-5, 2014, pp. 771-780

Acknowledgement

“Supported by grant from EEA and Norway Grants. The research was performed during the Concrete Innovation (COIN) programme, see www.coinweb.no.”

Ceramic concrete – vision and experience

Milan Kekanovic
Faculty of Civil Engineering, Subotica, Serbia, kekec@gf.uns.ac.rs

Abstract

Ceramic aggregates represent an innovative type of filler into concrete, which was likely also used in the ancient past. Ceramic aggregates can replace river and crushed stone and silica sand in fine fractions, which are commonly applied in the concrete production now.

1 Introduction

Basic characteristics of laboratory tested ceramic aggregate Subotica are: bulk density - 1880 kg/m^3, specific gravity - 2590 kg/m^3, open porosity - 27.41°C water absorption capacity – 14.23 %, average compressive strength 34 MPa. The aggregate consists of 61.86 % SiO_2, 16.68 % Al_2O_3, 5.76 % Fe_2O_3, 7.87 % CaO, 3.24 % MgO, 1.38 % Na_2O and 2.83 % K_2O. The sample of ceramic aggregate obtained from the crushed ceramic tiles is shown in Figure 1.

2 Results and discussion

The following properties have been confirmed as preferred: strength increase during hydration time as the result of pozzolanic activity contributes to the improved resistance and durability; lower bulk density; better thermo-insulating characteristics. A disadvantage may be considered: rather low frost resistance as well as large shrinkage and crack propagation if water absorption of the ceramic aggregate is unsatisfactory; and higher price of ceramic concrete opposite to modern traditional concretes.

Figure 1 Ceramic aggregate for use in ceramic concrete

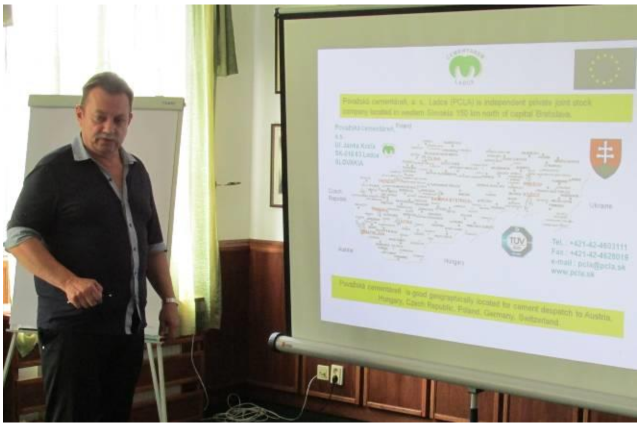
3 Conclusions

As further improvement of ceramic concrete quality are considered: - production of pozzolanic active aggregate with compressive strength > 100 MPa and water absorption < 5 % and pozzolanic activity secured by high percentage contents of SiO_2 and Al_2O_3; next appreciation by achieving compressive and tensile strength > 200 MPa and > 20 MPa, for use in high-durable structural concretes (tall buildings, large bridges, highways, etc...).

Acknowledgement

"Supported by a grant from EEA and Norway Grants."

CEMENTÁREŇ
LADCE



Success driven by innovations since 1889

Pavel Martauz
Považská cementáreň, a. s., Ladce cement plant, martauz.p@pcla.sk

Abstract

Figure 1 illustrates 3-years increase in the own cement and concrete production.

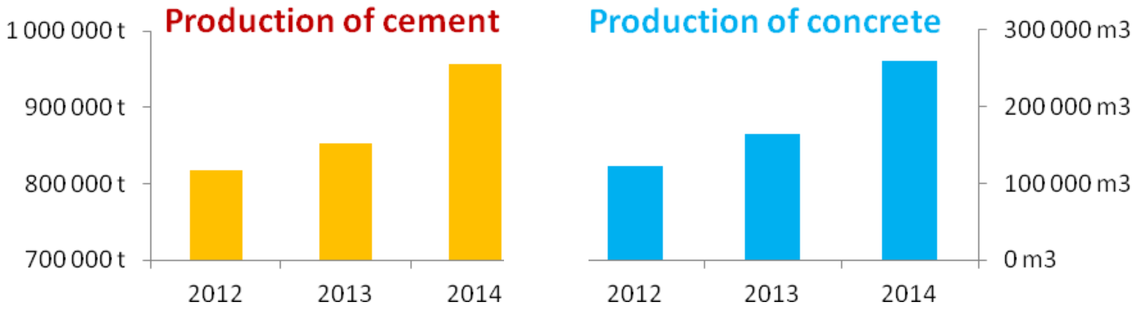


Figure 1 Growth in the production of cement and concrete in own concrete plants

1 Introduction

Process and quality management system in the cement plant is secured by: good raw material basis; unique reactivity model of limestone blend directly in quarry; long term control of clinker mineralogy using optical microscopy and XRD; patented technology OPTIMAX for fast intervention to clinker mineralogy directly in the kiln; on-line sampling and measurements since 2013; 24-hours control and monitoring in laboratory information management system; high demands on laboratory staff and technical support of sales department and clients.

2 Discussion and conclusion related to new generation of the cements

The cements are produced by mechanical - chemical activation enabling to work at industrial conditions on the nanolevel technology with new added values of the final products. The last cement innovations emphasising one of the confirmed key utility property are:

H-CEMENT	Shrinkage reducing cement
NONRIVAL	Sulphate resisting cement
CHAMPION	Ultrahigh performance cement

Acknowledgement

“Supported by a grant from EEA and Norway Grants.”

Long-term sulphate resistance of C_3A - containing cement NONRIVAL of Ladce provenance

Michal Bačuvčík
Building Testing and Research Institute, Bratislava, Slovakia, bacuvcik@tsus.sk

Abstract

Nonrival is novel high-strength CEM I cement of class 52.5 N, manufactured by the new technology of mechano-chemical activation of pozzolan to the nanoparticle size level. The cement contains more than 7 mass % of C_3A in the cement clinker. The composition of Nonrival is compliant with the requirements given on cements according to STN EN 197-1[1].

1 Introduction

During the last 30 years concrete is changed in composition and performance: only a minor part of cement is still Portland cement. In Europe about 90 % of the cement adopted in modern concretes is in form of blended cements where Portland cement is replaced by natural and industrial pozzolan. Concurrent use of chemical admixtures and particularly superplasticizers has revolutioned technology of concrete in terms of workability, high strength and durable concrete[2]. Sulphate attack is described as a series of chemical reactions between sulphate ions and the components of hardened concrete, principally cement paste and mainly C_3A[3]. This paper shows Nonrival containing > 7 mass % C_3A as sulphate-resisting cement. Sulphate resistance was investigated by partial accelerated degradation test according to the methodology of TSÚS.

2 Results and discussion

2.1 Basic properties of cements

Nonrival (NON) is characterized by the largest specific surface area and strengths compared to the sulphate resisting cement CEM I 42.5 R - SR 0 (SRC) and ordinary Portland cement CEM I 42.5 R (OPC). Cements differ in C_3A content (*Table 1*).

Table 1 Basic properties of cements and mortars

Cement kind	C_3A content (%)	Specific surface area (m^2/kg)	Compressive strength (MPa)		Flexural strength (MPa)	
			2-day	28-day	2-day	28-day
NON	7.94	766.9	37.1	72.2	7.4	8.5
SRC	0.03	354.9	26.2	52.8	4.7	8.4
OPC	14.31	472.4	31.5	58.0	6.2	8.5

2.2 Sulphate resistance

Cement mortars made with Nonrival and SRC showed only negligible expansion after 2.5 years exposure in aggressive 5 % sodium sulphate solution opposite to the mortar made with OPC, confirming evident expansion (*Fig. 1*). No significant difference in dynamic module of elasticity of the mortars with Nonrival and SRC kept in water and sulphate exposures were recognized while those in the mortar containing OPC were in sodium sulphate markedly decreased (*Fig. 2*).

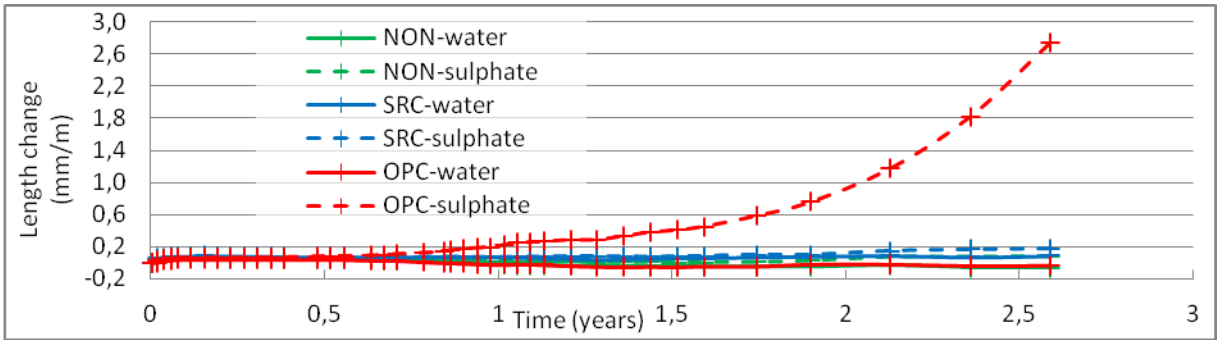


Figure 1 Length changes of mortars with NON, SRC and OPC during long-term curing in water and sodium sulphate solution

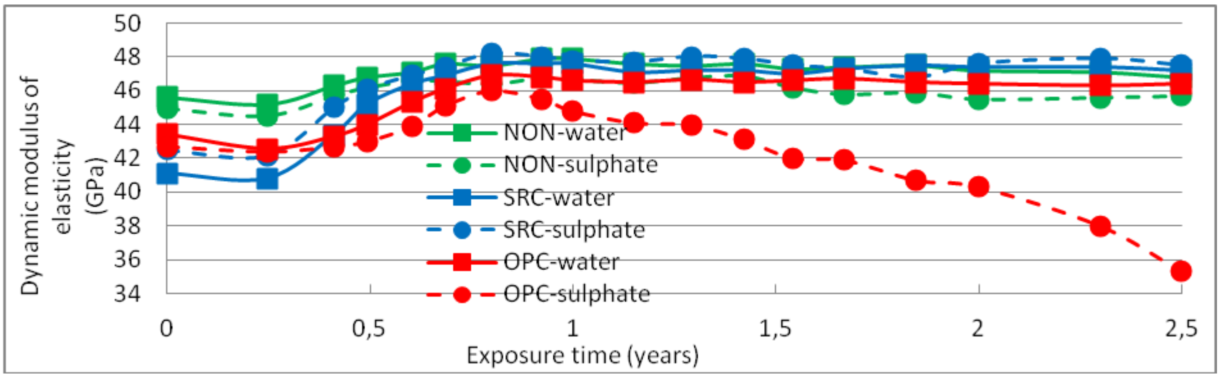


Figure 2 Dynamic modulus *of elasticity of mortars with NON, SRC and OPC during long-term curing in water and sodium sulphate solution*

3 Conclusions

Mechanical, microstructure and pore structure properties and visual examination show the same sulphate resistance of Nonrival as sulphate resisting cement of CEM I 42.5 R - SR 0. Nonrival activated on nanoparticles containing over 7 mass % of C_3A is intended for use in high strength class structural concrete exposed to natural sulphate-aggressive environments.

References

1) STN EN 197-1: 2012 Cement. Part 1: Composition, specifications and conformity criteria for common cements.
2) Collepardi, M.: "The New Concrete", (ed.) Grafiche Tintoretto, Castrette di Villorba TV, Italy, October 2006, 421 p.
3) Skalny, J., Marchand, J. and Odler I.: "Sulphate Attack on Concrete", (ed) SPON Press, Taylor & Francis Group, Series of books on Modern Concrete Technology edited by A. Bentur and S. Mindess, London and New York, 2002, 217 p.

Acknowledgement

"Supported by a grant from EEA and Norway Grants."

Key utility properties of hybrid cement of Ladce provenance

Ivan Janotka
Building Testing and Research Institute, Bratislava, Slovakia, janotka@tsus.sk

Abstract

The novel hybrid cement (H-Cement) is composed of fly ash, granulated blast furnace slag, precipitated alkaline waste water concentrate from bauxite residues deposit as amorphous inorganic-based geopolymer and 20 mass % of Portland cement clinker in maximum. H-Cement represents a transition stage between conventional cement and a geopolymer system with the advantage of not requiring any heat treatment and autoclaving, so as the cements according to EN 197-1 Standard[1].

1 Introduction

Main task of the present research is the development of less energy intensive and more environmentally acceptable cements. One possible solution is the development and production of hybrid cements with low Portland cement clinker content. Despite low clinker content, hybrid cements can attain useful early and long-term mechanical properties[2, 3].

2 Results and discussion

2.1 Ready-mixed concrete

H-Cement is suitable for ready-mixed concrete between C8/10 and C30/37 strength class[4]. Lignosulfonates, polycarboxylates as chemical admixtures alone and combined are the best appropriate plasticizers for use with H-Cement due to the most prolonged workability 60-minutes after mixing a fresh concrete mixture.

2.2 Durability

H-Cement shows improved sodium sulphate resistance compared to OPC. Microstructure of mortars with H-Cement is deteriorated to the less extent by magnesium chloride and hydrochloride acid attack compared to OPC mortar. The above findings insert this low-energy and environmentally-friendly hybrid cement to the group of special cements showing better chemical resistance relative to that of OPC[5].

2.3 Shrinkage-reducing properties

90-days shrinkage of H-Cement concrete is reduced by 48.0 % in 20 °C/ 60 % R. H. (*Fig. 1*) and 58.4 % 40 °C/15 % R.H.-dry air cure opposite to OPC concrete. It is thought that shrinkage-reducing character of H-Cement is primarily caused by 68.29 % drop in clinker minerals content relative to that in OPC.

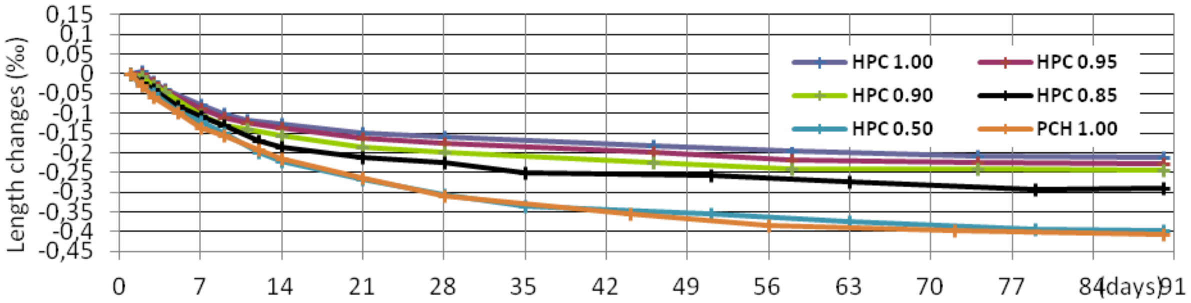


Figure 1 Length changes of concretes of the same composition in 20 °C/60 % R.H. - air cure

2.4 Elimination of alkali-aggregate reaction (AAR)

H-cement eliminates alkali-aggregate reaction to almost non-expansionable level at 20 °C (*Fig. 2*) and 40 °C/100 % - wet air cure. This statement is still valid after last-done 9-months measurements performed in April 2015 on the mortars of size (40 × 40 × 160) mm.

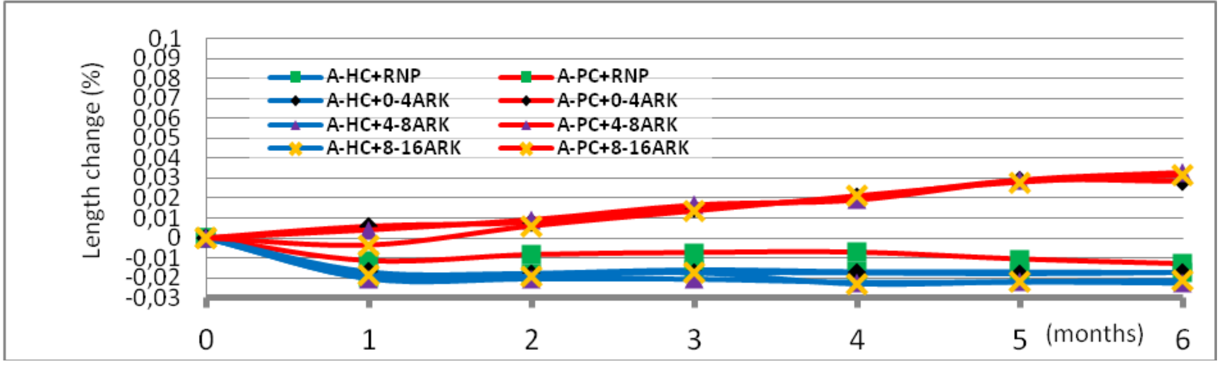


Figure 2 Expansion of alkali-activated cements to the value of 1.30 ± 0.5 % $Na_2$0 equivalent

3 Conclusions

The present state of development shows suitability of H-Cement for concrete and ready-mixed concrete mainly of low hydration heat and strength classes between C8/10 and C30/37 with improved chemical resistance, shrinkage-reducing and AAR - suppressing properties as well as its low-cost way of industrial production in Považská cementáreň cement plant.

References

1) STN EN 197-1: 2012 Cement. Part 1: Composition, specifications and conformity criteria for common cements.
2) Fernández-Jimenénez A., Sobrados I., Sanz I., and Palomo A. “Hybrid cements with very low OPC content”, In: Palomo A (ed.) Proceeding of 13th international congress on the chemistry of cement, Madrid, Spain, 3 - 8 July 2011, pp 1-7.
3) Palomo A, Krivenko P, García-Lodeiro I, Kavalerova E, Maltseva O, and Fernández-Jimenénez A.: “A review on alkaline activation: new analytical perspectives”, Materiales de Construcción, 2014, 64 (315): e022.
4) STN EN 206-1: 2002 Concrete. Part 1: Specification, performance, production and conformity.
5) Janotka, I., Bačuvčík, M., Martauz, P. and Strigáč, J.: “Chemical resistance of novel hybrid cement in various aggressive solutions. In: Bjegović, D., Beushausen, H., Serdar, M. (eds.) Proceedings of RILEM workshop on performance-based specification and control of concrete durability, Zagreb, Croatia, 11- 13 June 2014, pp 17-24.

Acknowledgement

“Supported by a grant from EEA and Norway Grants.”

WORKSHOP BENEFITS

Strengthening bilateral relations: The investigators of Building Testing and Research Institute (TSUS) Bratislava, Dr. Ivan Janotka and Dipl. - Ing. Michal Bačuvčík and those of SINTEF Building and Infrastructure Trondheim, B.Sc. Tone Anita Østnor and Professor Harald Justness, Považská cementáreň, a. s. cement plant Ladce (PCLA), Dipl. - Ing. Pavel Martauz as well as Institute of Inorganic Chemistry, Slovak Academy of Sciences Bratislava, Dr. Jana Madejová, DSc. and Dr. Peter Komadel, DSc. have created strong and creative scientific team based on mutual understanding and friendship.

Achieving the goal in the specific topic: Progress in the development of cement of new generation with unusual and previously disused raw material in Slovakia – marl, whose deposit is owned by PCLA. Slovak partners took 2-years research experience of SINTEF gained with marl of Norwegian origin and informed SINTEF people on the development of new generation cements based on inorganic polymer (hybrid cement) and superior properties cement based on industrially applied nanotechnology (special cement). These three basic kinds of cements represent developmental products to become a sophisticated alternative for the present range cements and are expected to appear on the market in the near future. New generation cements are pushing into practice the current economic and environmental requirements - cheaper but technically good and environmentally preferred cement.

Target value of activity implementation: Mutual knowledge sharing, contribution to knowledge and subsequent direction of development of new generation cements with main future emphasis on use of marl as major raw material required for manufacturing cement of new generation as energy-saving and environmental - friendly cement in Norway and Slovakia. All parties involved have expressed their agreement for further continuation of the present cooperation, preferably in joint international project.

„NOVACEM project was s*upported by a grant from EEA and Norway Grants.“*

TECHNICKÝ A SKÚŠOBNÝ ÚSTAV STAVEBNÝ
BUILDING TESTING AND RESEARCH INSTITUTE

www.tsus.sk

„Supported by a grant from EEA and Norway Grants“.