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10th ACI/RILEM International
Conference on Cementitious
Materials and Alternative Binders
for Sustainable Concrete

Editor:
Arezki Tagnit-Hamou

SP-320



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Preface

In July 1983, the Canada Centre for Mineral and Energy Technology (CANMET) of Natural Resources Canada (CANMET), in association with the American Concrete Institute (ACI) and the U.S. Army Corps of Engineers, sponsored a 5-day international conference at Montebello, Quebec, Canada, on the use of fly ash, silica fume, slag and other mineral by-products in concrete. The conference brought together representatives from industry, academia, and government agencies to present the latest information on these materials and to explore new areas of needed research. Since then, eight other such conferences have taken place around the world (Madrid, Trondheim, Istanbul, Milwaukee, Bangkok, Madras, Las Vegas, and Warsaw). The 2007 Warsaw conference was the last in this series.

In 2017, due to renewed interest in alternative and sustainable binders and supplementary cementitious materials, ACI and the International Union of Laboratories and Experts in Construction materials, Systems and Structures (RILEM)—in association with a number of other organizations in Canada, the United States, and the Caribbean—sponsored the 10th ACI/RILEM International Conference on Cementitious Materials and Alternative Binders for Sustainable Concrete (ICCM2017).

The purpose of this international conference is to present the latest scientific and technical information in the field of supplementary cementitious materials and novel binders for use in concrete. The new aspect of this conference is to highlight advances in the field of alternative and sustainable binders and supplementary cementitious materials, which are receiving increasing attention from the research community. The conference was held in Montréal, Canada from October 2 to 4, 2017. The conference proceedings, containing 50 refereed papers from more than 33 countries, were published as ACI SP-320.

To all those whose submissions could not be included in the conference proceedings, the Institute and the Conference Organizing Committee extends its appreciation for their interest and hard work. A large number of other papers were presented in addition to those published in the proceedings. Most of these were published as supplementary papers, and the authors have been encouraged to publish them in technical journals of their choosing.

Thanks are extended to the members of the Technical Paper Review Panel that met in March 2017 to review the papers. Without their dedicated effort, the proceedings could not have been published for distribution at the conference. The cooperation of the authors in accepting reviewers' suggestions and revising their manuscripts accordingly is greatly appreciated. Special thanks go out to Mohan Malhotra, the conference's past chair, for sharing his extremely extended knowledge about organizing this kind of conference with the organizing committee.

The help and assistance of Bianca Roy at the Université de Sherbrooke are gratefully acknowledged for the administrative work associated with the conference and for processing the manuscripts both for the ACI proceedings and the supplementary volume. Thanks are also extended to Pierre-Claver Nkinamubanzi, Chair of the Audio-Visual Review Panel, for his services to ensure that the visuals met ACI/RILEM criteria.

Arezki Tagnit Hamou, Editor

Chairman, Tenth ACI/RILEM International Conference on Cementitious Materials and Alternative Binders for Sustainable Concrete (ICCM2017).
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TABLE OF CONTENTS

SP-320—1

Activated Hybrid Cementitious System, a Green Alternative for Concrete Production

Authors: Diego Velandia, Cyril Lynsdale, John L. Provis, and Fernando Ramirez

SP-320—2

Preferable Use of Hybrid Cement in Concrete Intended for Industrial Applications

Authors: I. Janotka, P. Martauz, and Michal Bačuvčík

SP-320—3

Low-Energy Alinite Cement from Soda Sludge Waste

Authors: Gültekin O. Uçal, Mahdi Mahyar, Mustafa Tokyay, and İsmail Ö. Yaman

SP-320—4

Reuse of Ceramic Industry Sludge as a Component in Cement-Based Materials

Authors: M.I. Sánchez De Rojas, M. Frías, E. Sabador, C. Medina, E. Asensio, and J. Rivera

SP-320—5

Effects of Sol-Gel Derived Nano-Silica Suspensions in Cement Paste

Authors: Dulani P. A. Kodippili, Ehsan Rezabeigi, Michelle R. Nokken, and Robin Drew

SP-320—6

Rheological Behaviour of Alkali-Activated Slag Concrete

Authors: Francisca Puertas, María Del Mar Alonso, Manuel Torres-Carrasco, Belen González

Fonteboá, Iris González Taboada, Gemma Rojo, and Fernando Martínez-Abella

SP-320—7

Performance and Properties of Concrete Made with Calcined Clays

Authors: Nancy Beuntner and Karl-Christian Thienel

SP-320—8

Mitigation of Microcracking in Alkali-Activated Combined Slag and Fly Ash Concretes for Good Performance in Winter Conditions

Authors: Alexandre Rodrigue, Josée Duchesne, Benoit Fournier, and Benoit Bissonnette

SP-320—9

New Additions for the Design of Eco-Efficient Cements. Analysis of Pozzolanic Reaction Kinetics

Authors: Gabriel Medina, José María Medina, Isabel Sáez Del Bosque, Moisés Frías, María Isabel Sánchez De Rojas, and César Medina

SP-320—10

Drying Shrinkage in Alkali Activated Class C Fly Ash Mortars and the Mitigation Methods

Authors: Darshan Ballekere Kumarappa, Chathurani Chandrasiri, and Sulapha Peethamparan

SP-320—11

Durability Properties of Fly Ash Blended Cement Concrete in Inland Environment

Authors: Yunusa A. Alhassan and Yunus Ballim

SP-320—12

Influence of Supplementary Cementitious Materials on the Autogenous Self-Healing of Cracks in Cementitious Materials

Authors: Imane Salama, Benoît Hilloulin, Sonagnon Medjigbodo, and Ahmed Loukili

SP-320—13

Performances of Hemp Concretes: from Microscopic to Functional Properties

Authors: Guillaume Delannoy, Sandrine Marceau, Philippe Glé, Etienne Gourlay, Marielle Guéguen-Minerbe, Dinarzed Diafi, Issam Nour, Sofiane Amziane, and Fabienne Farcas

SP-320—14

New Insights into the Retarding Effect of Aluminates on C_3S Hydration

Authors: E. Pustovgar, M. Palacios, J.-B. D'espinoze De Lacaille, T. Matschei, N. Ruffray, R. Verel, and R.J. Flat

SP-320—15

Influence of Pozzolanic Materials on the Hydration of Calcium Sulfoaluminate Cements

Authors: Frank Winnefeld, Lukas H.J. Martin, Elsa Tschopp, Christian J. Müller, and Barbara Lothenbach

SP-320—16

Chloride Ingress in Concrete Containing GGBF Slag or Fly Ash

Authors: Eisuke Nakamura and Hirohisa Koga

SP-320—17

Modelling of Temperature-Dependent Pozzolanic Reaction of Low-Calcium Fly Ash in Blended Cement Paste

Authors: Tiao Wang, Tetsuya Ishida, and Yuya Takahashi

SP-320—18

Corrosion Resistance of Concrete Incorporating Supplementary Cementing Materials in a Marine Environment

Authors: Andrew Fahim, Edward G. Moffatt, and Michael D.A. Thomas

SP-320—19

Environmental Benefits of Using Glass Powder in Manhole Production

Authors: J.-M. Lessard, J. Cloutier, A. Tagnit-Hamou, and B. Amor

SP-320—20

Effects of Ternary Cements with Limestone Filler on DEF in Concrete

Authors: Yasser Amine, Nordine Leklou, and Ouali Amiri

SP-320—21

Carbonation-Activated Steel Slag Binder As Alternative Cementing Material

Authors: Yixin Shao, Mehrdad Mahoutian, and Zaid Ghoulleh

SP-320—22

A New Generation of Micro-Particulate-Based Admixtures for Concrete

Authors: Paul H. Seiler, Christopher Eagon, Frank S. Ong, Stephen A. Farrington, and Van Bui

SP-320—23

Assessing the Autogenous Shrinkage of Alkali-Activated Slag/Fly Ash Mortar Blends

Authors: Siva Uppalapati and Özlem Cizer

SP-320—24

Properties of Self-Compacting Concrete with Natural and Synthetic Fibers

Authors: Tahar Tioua, Abdelouahed Kriker, Abderrahim Bali, Gonzalo Barluenga, and Mourad Behim

SP-320—25

The Role of Surface Area and Compacity of Nanoparticles on the Rheology of Cement Paste

Authors: Oscar A. Mendoza Reales, Emílio C. C. M. Silva, Maria D. M. Paiva, Pedro Duda, and Romildo Dias Toledo Filho

SP-320—26

Comparison of Three Plasticizers in Carbonate-Activated Slag Concrete

Author: Rolf Andreas Lauten

SP-320—27

Mixture Proportions of Concrete with Dredging Sediments as Novel SCM

Authors: Céline Van Bunderen, Ruben Snellings, Liesbeth Horckmans, Lucie Vandewalle, and Özlem Cizer

SP-320—28

Monitoring the Hydration of Cementitious Material by Acoustic Emission

Authors: Evin Dildar Dzaye, Geert De Schutter, and Dimitrios Aggelis

SP-320—29

Chemo-Mechanical Properties of Cement Matrices with Fly Ash and Slag

Authors: William Wilson, Luca Sorelli, and Arezki Tagnit-Hamou

SP-320—30

Effects of Pre-Hydration on Compressive Strength of Quaternary Binders

Authors: Suguru Goto, Thomas A. Bier, Keisuke Takahashi, and Tetsuhiro Sakai

SP-320—31

Degree of Fly Ash Reaction in Internally Alkali-Activated Cement Paste

Authors: Phuong Trinh Bui, Yuko Ogawa, Kenichiro Nakarai, and Kenji Kawai

SP-320—32

Metakaolin-Based Geopolymer Concretes: From Dry to Fluid Concretes

Authors: Raphaëlle Pouhet and Martin Cyr

SP-320—33

Investigating the Feasibility of Using Reclaimed and Remediated Fly Ashes as Class F Fly Ash Alternatives

Authors: Raissa Ferron, Ryan Kalina, Saif Al-Shmaisani, and Maria Juenger

SP-320—34

Potential for Using Waste Recycled Glass in Engineered Cementitious Composites

Authors: Hocine Siad, Mohamed Lachemi, Mustafa Sahmaran, and K. M Hossain

SP-320—35

Suitability of Alkali Activated GGBS/Fly Ash Concrete for Chloride Environments

Authors: Dali Bondar, Sreejith V. Nanukuttan, Marios N. Soutsos, P.A. Muhammed Basheer, and John L. Provis

SP-320—36

Factors Controlling Carbonation Resistance of Alkali-Activated Materials

Authors: Susan A. Bernal, Xinyuan Ke, Maria Criado, Shishir Mundra, and John L. Provis

SP-320—37

Alkali-Activated Cementitious Materials and Concretes – Steps Towards Standardization

Author: John L. Provis

SP-320—38

Development of Test Methods and Specifications for Chemically Activated Binders

Authors: R. Douglas Hooton, Lawrence Sutter, and Mary Christiansen

SP-320—39

Isothermal Calorimetry Investigation of Slag Activation

Authors: Qiwei C. Nowasell, Ray B. Henderson, and John T. Kevern

SP-320—40

Industrial Production and Use of a Portland Calcined Clay Limestone Cement

Authors: Fernando Martirena and Karen Scrivener

SP-320—41

Towards a Service Life Prediction System of Concrete Structures Based on a Neural-Computing Approach
Authors: Bakhta Boukhatem, Arezki Tagnit-Hamou, Mohamed Chekired, and Mohamed Ghrici

SP-320—42

Large Amplitude Oscillatory Shear Protocol Applied to Cement-Based Materials
Authors: Théau Conte and Mohend Chaouche

SP-320—43

Delayed Ettringite Formation in Concrete Containing Limestone Filler
Authors: Mohammad A. Aql and Daman K. Panesar

SP-320—44

Geopolymers Cured at Ambient Temperatures
Authors: Daniela Hesselbarth, Thomas Moser, and Jürg Sturzenegger

SP-320—45

Effect of Glass Powder (GP) on the Pore Solution of Cement Pastes
Authors: Isabelle Fily-Paré, Benoît Fournier, Josée Duchesne, and Arezki Tagnit-Hamou

SP-320—46

Optimization Performance of High Volume Fly Ash Self-Consolidating Mixtures with Hydrated Lime (Mortar Component)
Authors: Hayder Alghazali and John J. Myers

SP-320—47

Thermal Behaviour of High Volume Fly Ash Concrete and Its Temperature Simulation
Authors: Peter G. Gaunt, Mathew K.R. Versfeld, André Ferreira, and Stephen O. Ekoru

SP-320—48

Influence of Lime on the Properties of Cement-Based Materials
Authors: Reda Jaafri, Abdelilah Aboulayt, Syed-Yasir Alam, Emmanuel Roziere, and Ahmed Loukili

SP-320—49

GGBS Cements Activated by Chloride: Hydration and Corrosion Potential
Authors: Laurent Steger, Bernard Salesses, Cédric Patapy, Mohend Chaouche, Laurent Frouin, and Martin Cyr

SP-320—50

Prediction of Hemp Concrete Morphological Deformation by X-ray Tomography
Authors: Kamilia Abahri, Chady El Hachem, Fares Bennai, Ngoc Toan, and Rafik Belarbi

ACTIVATED HYBRID CEMENTITIOUS SYSTEM, A GREEN ALTERNATIVE FOR CONCRETE PRODUCTION

Diego Velandia, Cyril Lynsdale, John L. Provis and Fernando Ramirez

Synopsis: Concretes made with blended portland cement containing high volumes of fly ash provide an alternative to conventional portland cement concrete for reducing CO₂ emissions. This study evaluates mechanical and chemical activation of four fly ashes by assessing their effects on hydration and compressive strength. Results show the importance of the amorphous content in terms of compressive strength. The composition of fly ash is changed by a sieving process where certain particle sizes are retained; the amorphous silica and loss on ignition (LOI) contents varied depending on the fineness, hence affecting the performance of the fly ash in concrete. Reduction in particle size and LOI do not always lead to improvement in compressive strength. The effect of sodium sulfate, as activator, was significant at early ages for two of the fly ashes studied; the amount of portlandite consumption is reflected in the compressive strength evolution observed. However, sodium sulfate does not have the same effect on fly ashes with high amount of Fe₂O₃, where portlandite consumption is much lower.

Keywords: Amorphous content, portlandite, sodium sulfate

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INTRODUCTION

Alternative materials to reduce the carbon footprint of the cement and concrete industries have been widely studied in recent years [1-15]. Among the alternatives, the inclusion of high volume fly ash concretes, or 100% slag or fly ash concretes are some of the most viable options [3-4]. This work is focused on a hybrid system with 50% normal portland cement, 50% fly ash and sodium sulfate as an activator. Although in most research studies this system is seen to be technically viable, there are still questions about what really affects its performance, from the material technology to the concrete mixture proportion.

Different fly ashes and activators including sodium sulfate, quicklime and lime are evaluated. Fly ash fineness and composition are related to mortar microstructure using X-ray fluorescence, X-ray diffraction and scanning electron microscopy analyses. The final objective is to identify the parameters influencing material performance and finding the most viable system.

RESEARCH SIGNIFICANCE

The use of geopolymers is an alternative for sustainable concrete production. Although it is a suitable alternative, there are still tendencies in the concrete industry that do not allow the move towards the use of geopolymers because of curing at high temperature. Therefore, it is important to evaluate an intermediate alternative where a high volume fly ash system (50% normal portland cement – 50% FA) is used with different activators (sodium sulfate, lime and quicklime). Based on results from mortar specimens, the most influential fly ash and activator parameters are presented.

EXPERIMENTAL INVESTIGATION

Materials

Four different fly ashes were used in this study, referenced as TP FA, FB FA, TG FA and TA FA. The three activators used were sodium sulfate, lime and quicklime. The four fly ashes were sieved (<74 μm and <45 μm), changing their composition by removing certain particle sizes. The cement used for this evaluation was a Type III cement (high early compressive strength) according to ASTM C 150 [16]. For the chemical analysis of the materials a PANalytical Axios sequential wavelength XRF was used, and XRD was used for the mineralogical analysis via a PANalytical XRD X-‘PERT-PRO MPD system.

As mentioned, the original granulometry of the fly ash was affected by the sieving process. Table 1 summarizes the effect on the main parameters. By sieving the material, not only did the particle size decrease but also the LOI content was reduced.

OS (original size) TA FA has the lowest LOI and the highest SiO_2 amongst all the fly ashes; this is due to the fact of being a commercial fly ash and the treatment (i.e LOI reduction) it receives by the fly ash supplier. In contrast, OS FB FA includes the highest LOI and lowest SiO_2 content, due to the burning system used by the energy producer and the fact of not being improved by a treatment.

Specimens

Although most of the procedures presented in ASTM C 109 [17] concerning sample preparation were followed, specific considerations adopted are mentioned below:

1. The activator was added to water; it was mixed until it was completely dissolved. Cement was added to the mixture of water and activator; it was mixed for 30 seconds at the lowest velocity of the mixer (level 1). After that, sand was added and mixed for 30 seconds. Then, it was left for 90 seconds. The fresh mortar was mixed again for 90 seconds at the medium velocity setting.
2. Sodium sulfate and lime had good solubility, while quicklime in contact with water increased the temperature and formed white solids (calcium hydroxide). This effect increased when the dosage was increased.
3. Samples were left in the curing room at a temperature of 23°C (73.5°F) until the day of the test.

Table 2 presents all the variables considered in the study and codes identifying the mixtures. Figure 1 presents all the different parameters evaluated in mortars and pastes with materials and dosages.

ANALYTICAL INVESTIGATION

Fly ash concrete research has focused on two main aspects in recent years: the use of high-volume fly ash (40%-60%) concrete, and geopolymer concrete using 100% fly ash or slag and a chemical activator. When a high volume fly ash concrete is proportioned, it is necessary to consider water-cementitious material ratio reduction; as it is reduced a superplasticizer is used to keep the same slump [3-5]. Although it is a green alternative, setting time and early strengths may be affected, becoming at some point critical issues to be controlled. Researchers have also studied the possibility of using 100% fly ash including an activator [6]; these studies show the necessity of including high-curing temperatures in order to reach the target strength for many ashes with low reactivity or where a hydroxide activator is selected, which makes such mixtures unviable for structural concrete production [16]. Intermediate mixtures, where the percentages are between 50% and 100%, have not presented successful behavior [17], in terms of setting time, rheology, early strength evolution, a specific 28 day strength accomplishment and cost. Therefore, it is important to establish the effect of different fly ash reactive silica and alumina content, and activator dosage on high-volume fly ash concrete.

EXPERIMENTAL RESULTS AND DISCUSSION

Results present how compressive strength varies depending on fly ash amorphous content. The composition of fly ash changed by increasing its fineness with a sieving process; the amorphous silica and LOI contents were different for each fineness. Figure 2 shows how the compressive strength of mortar samples with 20% fly ash was improved when the amorphous content increased; for TP FA and TG FA when the particle size and the LOI content decreased, the compressive strength decreased because the amorphous content was lower.

Considering the interaction with activators at different dosages, TP FA had an acceptable performance with sodium sulfate at a dosage of 1%; according to Fig. 3a, compressive strength increased by about 40% compared to the similar concrete without activator. Initially it was expected that as a commercial fly ash, TA FA would have the best performance when activated, but this ash actually did not react as well as FB FA, as presented in Fig. 3b; possibly it is due to the highest Fe_2O_3 content reducing the rate of dissolution of the reactive components of fly ash and/or the degree of aluminosilicate gel formation. On the other hand, FB fly ash had the lowest Fe_2O_3 and exhibited the highest compressive strength using sodium sulfate as activator.

Based on thermogravimetry results (Fig. 4a), it was evident that mixtures including sodium sulfate consumed more $\text{Ca}(\text{OH})_2$ with time; $\text{Ca}(\text{OH})_2$ quantification was similar using both thermogravimetry and XRD. Portlandite reduction with sodium sulfate and TP FA started at the age of 3 days followed by FB FA at 7 days. Figure 4b shows how portlandite content for mixtures with TG FA increased from 3 to 28 days. Portlandite production in mixtures including lime and quicklime generally kept increasing after 7 days.

Ettringite and the amorphous content determined using XRD were consistent with the compressive strength evolution; at the early ages the formation of ettringite helped to improve the compressive strength and at later ages the formation of C-S-H increased, partly due to the increase in the amorphous content, as presented in Table 3.

Figure 5 shows ettringite formation over the TP FA surface at the ages of 7 and 28 days in a mixture with 50% fly ash and sodium sulfate. The presence of portlandite and C-S-H is also evident in these SEM images.

CONCLUSIONS

According to the results, the amorphous content of fly ash was the most influential factor for the compressive strength for mixtures with low fly ash content (20%) and without any activator. By improving fly ash fineness its composition changed; the amorphous silica and LOI contents varied depending on the fineness. The compressive strength of mortar samples was improved when the amorphous content increased; in some cases when the particle size and the LOI content decreased, the compressive strength decreased, which occurred probably because the amorphous content was low. Depending on the initial amorphous content, fly ash may not need mechanical treatment to improve its reactivity for use in such high volume blends.

For mixtures with activators, the effect of sodium sulfate in mixtures with TP FA and FB FA was significant at the initial stages of the reaction. The amount of ettringite and the accelerated portlandite consumption were reflected in the compressive strength evolution. On the other hand, sodium sulfate did not have the same effect on TG FA and TA FA; the amounts of ettringite and portlandite consumption were not as significant as those for the first two fly ashes. This was probably due to the higher amount of Fe_2O_3 present in the TG and TA fly ashes.

In general, different activators were evaluated and mixtures with sodium sulfate presented an acceptable behavior compared to the control sample. In the case of fly ashes, the commercial one (treated to reduce LOI) did not perform as expected, probably due to its high Fe_2O_3 content. Initially the low fineness of TP and FB fly ash and their high LOI content were seen as possible activation problems, but it was found that the main influencing factors were the reactive alumina and silica contents and the amount of Fe_2O_3 .

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TABLES AND FIGURES

Table 1– Fly ash composition

Fly ash	Sieve - Treatment	Main Parameters				
		LOI	Fe ₂ O ₃	CaO	SiO ₂	Amorphous
TP	As received	10.7	4.9	3.3	56.7	64.5
	< 74 μ m	8.7	5.9	0.6	59.5	67.3
	< 45 μ m	5.1	5.3	1.4	62.3	59.6
FB	As received	12.0	4.4	6.0	43.8	69.3
	< 74 μ m		3.8	3.2	45.0	60.2
	< 45 μ m	5.8	4.8	6.9	45.4	63.6
TG	As received	8.7	9.8	3.6	55.1	65.6
	< 74 μ m	1.5	11.2	2.6	63.1	56.1
	< 45 μ m	1.9	10.5	4.4	56.9	65.5
TA	As received	1.5	10.2	3.2	58.6	76.0
	< 74 μ m	1.3	10.7	3.0	57.9	75.5
	< 45 μ m	1.5	10.4	2.8	56.6	78.1

Table 2– Mixture ID: a) order and description; b) code for each variable

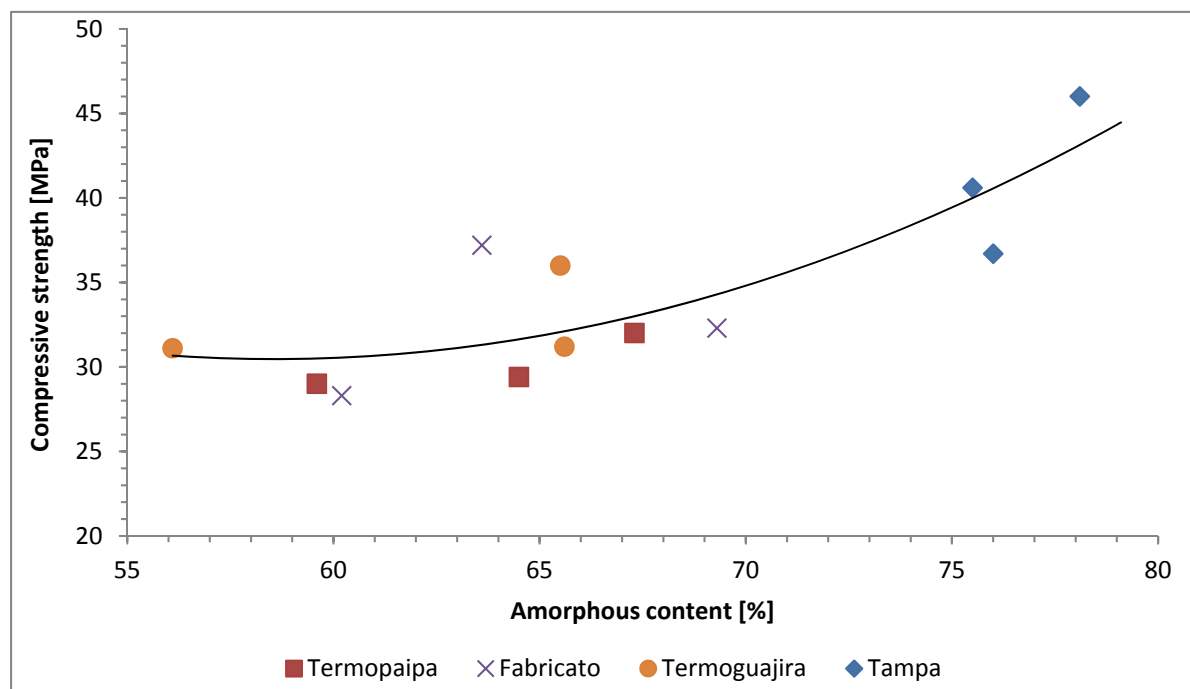
Mix ID (1/2/3/4/5/6)	
Letters and numbers order	Description
1	Cementitious material name
2	Cementitious material size
3	Cementitious material percentage
4	Activator
5	Dosage (%)
6	Age – Days
1 - Cementitious material Name	
CE	Cement
TP, FB, TG, TA	Fly ash
2 - Size	
10	D50 - Cement
OS	Original Size - Fly ash
3 - Cementitious material percentage	
0	0%
20	20%
50	50%
100	100%
4 - Activators	
A	Sodium sulfate
Q	Quicklime
L	Lime

Table 3– XRD analysis of fly ashes with sodium sulfate at 1% at 3, 7 and 28 days

Mixture ID	Quartz low	Tobermorite 9Å	Mullite	Portlandite	Ettringite	C ₂ S+C ₃ S	C ₃ A	Amorphous content
TP/OS/50/A/1/7	8.3	5.4	7.6	5.7	5.8	3.80	0.2	57.7
TP/OS/50/A/1/3	7.3	7.4	7.8	6.0	5.6	4.30	0.2	58.1
TP/OS/50/A/1/28	5.76	8.08	5.35	2.65	2.17	2.44	0	71.39
TG/OS/50/A/1/7	6.9	5.06	2.69	7.19	2.18	7.71	0.27	67.99
TG/OS/50/A/1/3	4.84	3.69	2.41	5.46	2.52	8.15	0.57	72.37
TG/OS/50/A/1/28	5.53	6.75	2.12	5.18	1.82	3.36	0.03	75.22
TA/OS/50/A/1/7	8.51	8.49	4.57	9.38	1.06	7.85	0.15	60
TA/OS/50/A/1/3	7.99	6.37	4.73	7.9	1.09	10.69	0.49	60.74
FB/OS/50/A/1/7	2.4	6.6	9.1	3.6	4.8	3.87	0.2	65.2
FB/OS/50/A/1/3	2.5	4.8	8.2	3.7	4.3	4.47	0.3	69.2
FB/OS/50/A/1/28	2.58	11.37	7.37	2.61	2.9	3.61	0.07	66.9

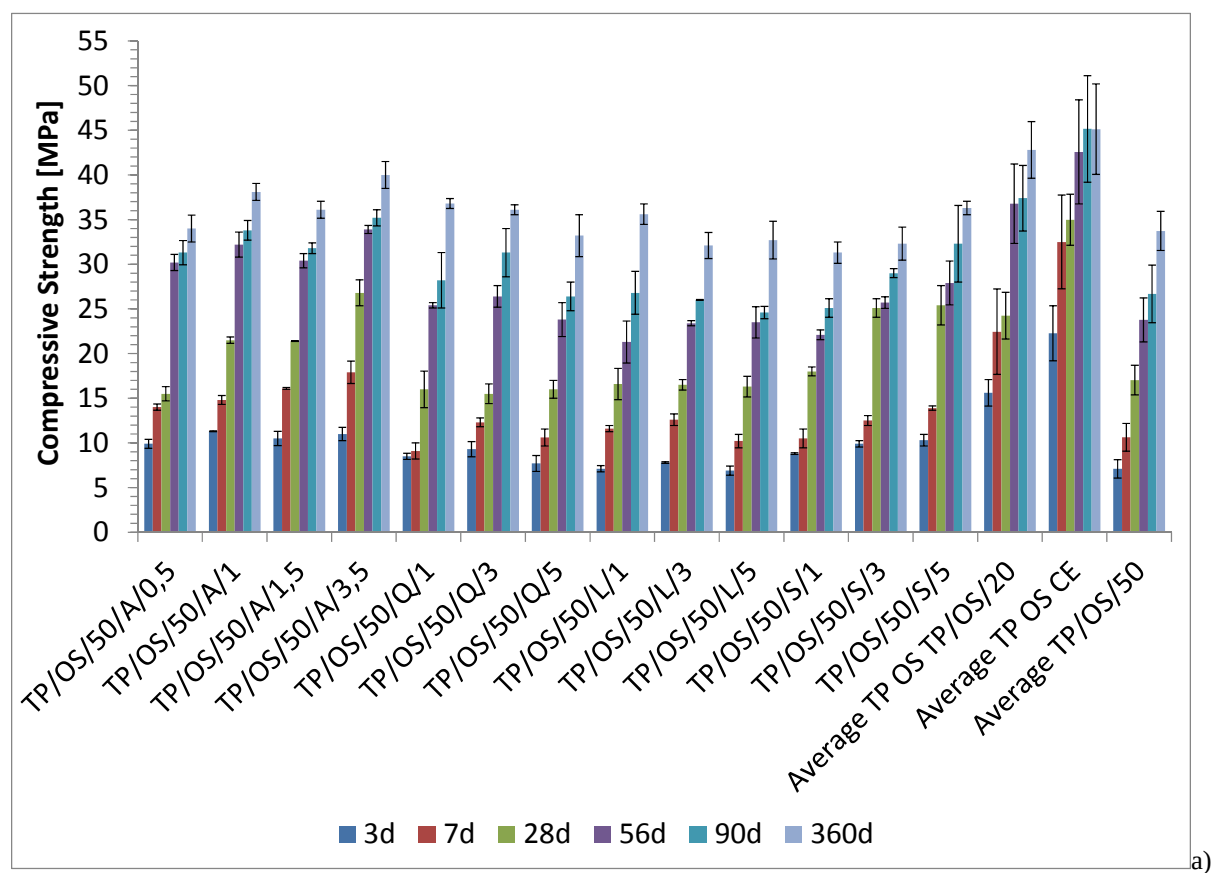
Mortars evaluation		Pastes evaluation		Activity
SCM: 50%				Constants
SCM's: TP FA, FB FA, TG FA, TA FA SCM's particle size: Original size, <75um, <45um Activator 1 Na2SO4 (0%, 0.5%, 1%, 1.5%, 3,5%) Activator 2 (0%, 1%, 3%, 5%) Activator 3 (0%, 1%, 3%, 5%) Hydrated lime Quicklime				Variables
Compressive strength	Mineralogy	SEM	Thermogravimetry	Evaluation

Fig. 1– Mortar and paste tests



[1 MPa = 145.038 psi]

Fig. 2– Influence of the amorphous content on the compressive strength



a)

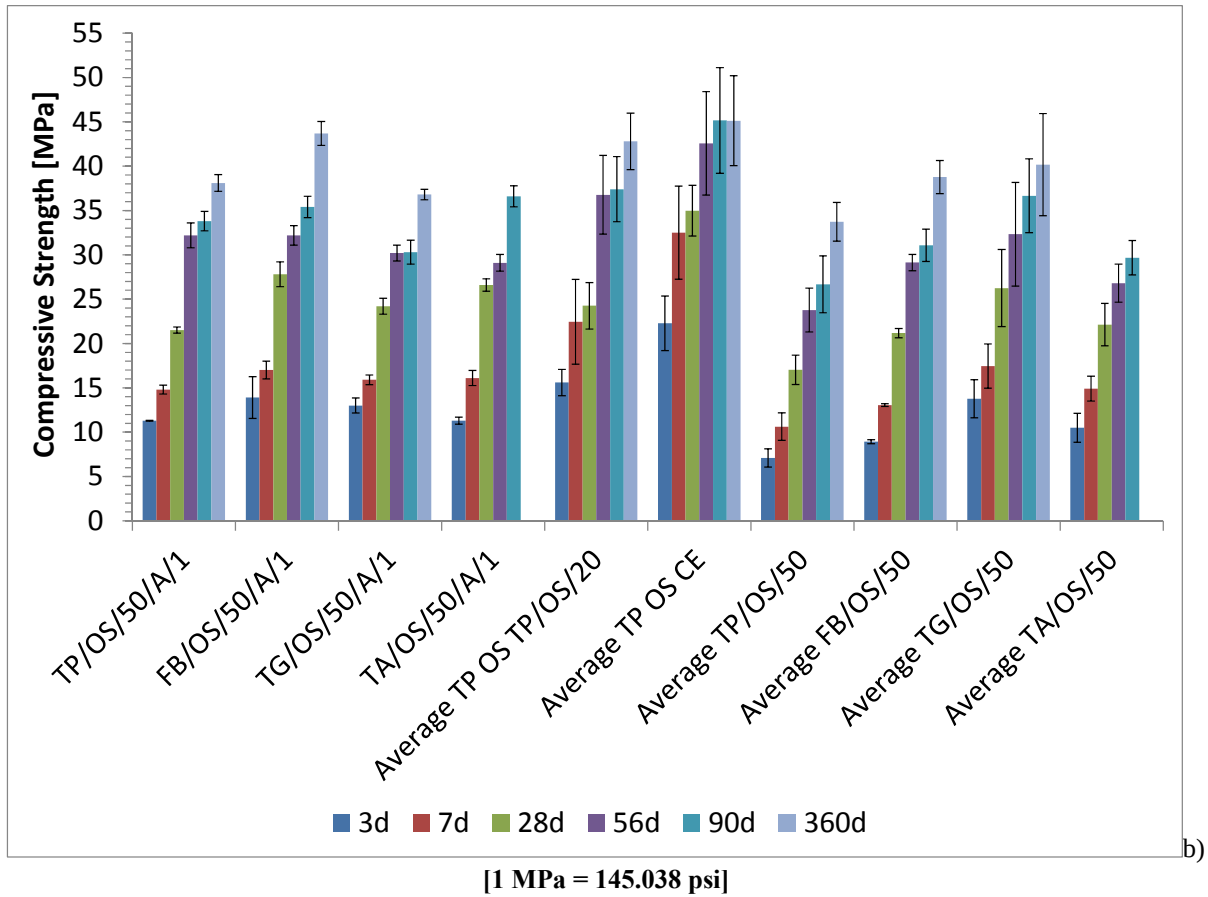
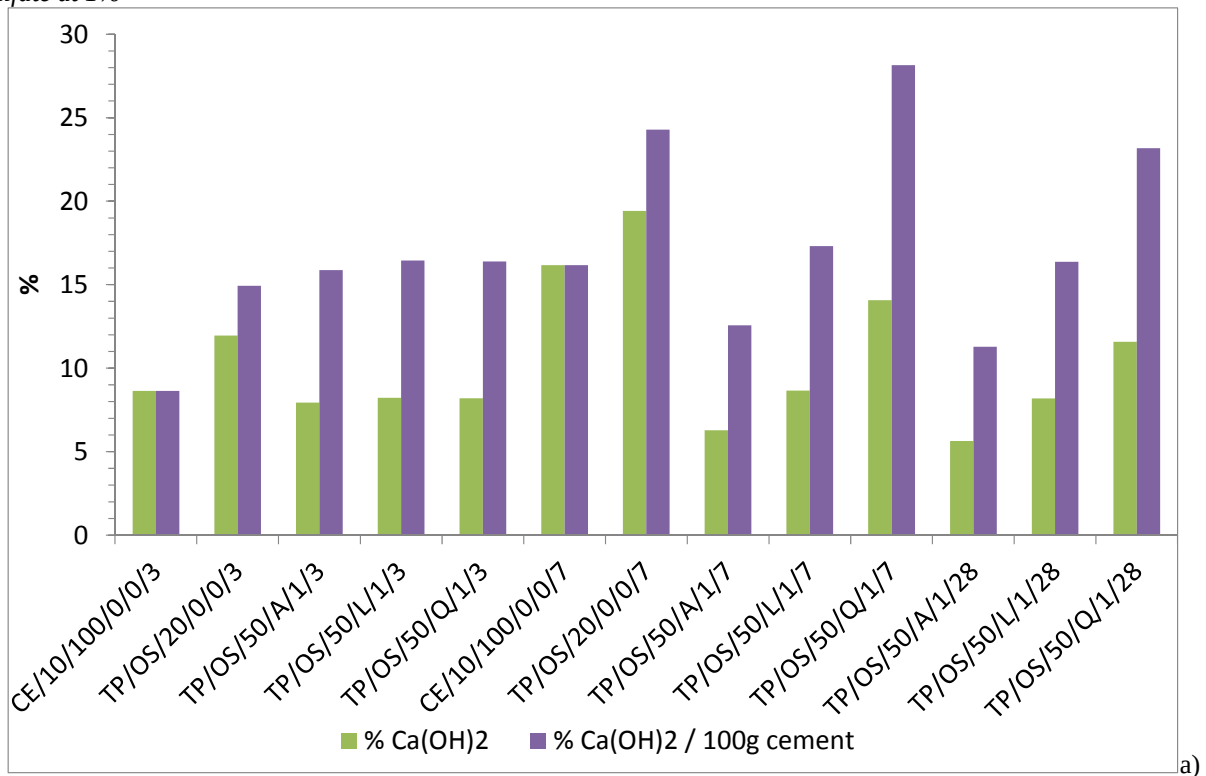


Fig. 3—Compressive strength evolution, a) TP FA with sodium sulfate, lime and quicklime; b) fly ashes with sodium sulfate at 1%



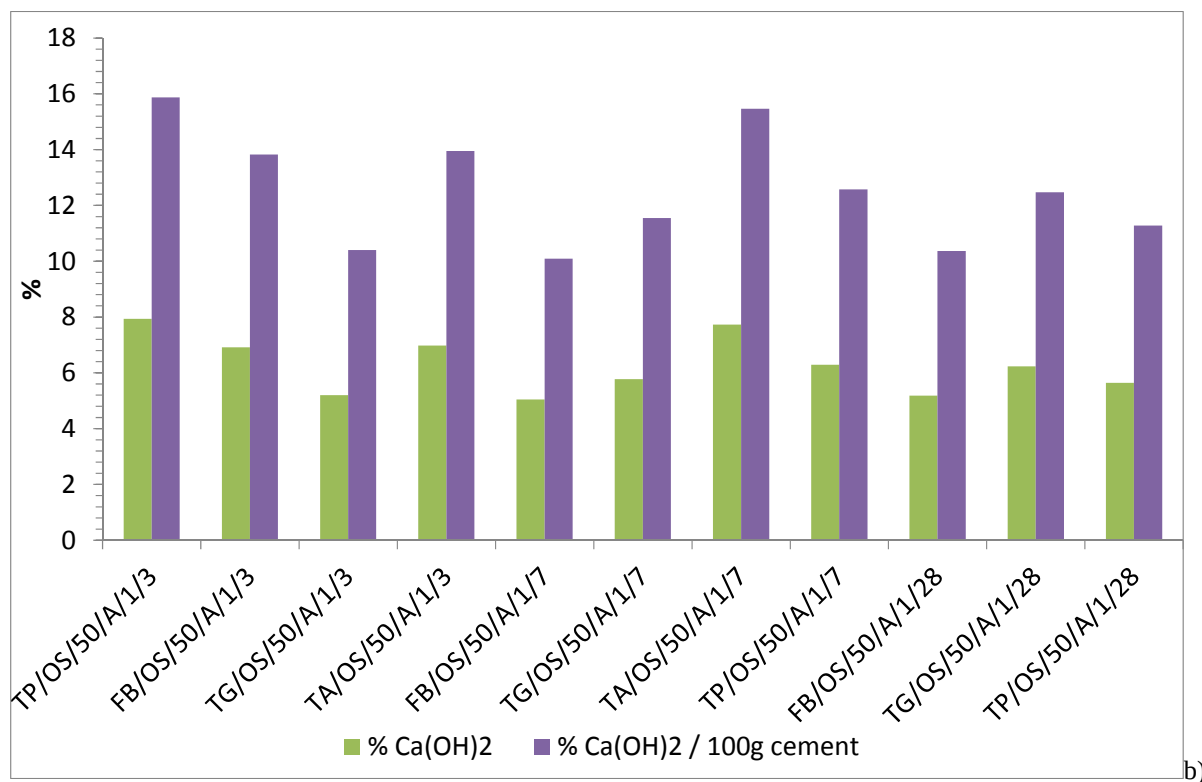


Fig. 4– Ca(OH)_2 content using TGA, a) TP FA with sodium sulfate, lime and quicklime; b) fly ashes with activator 1 at 1%

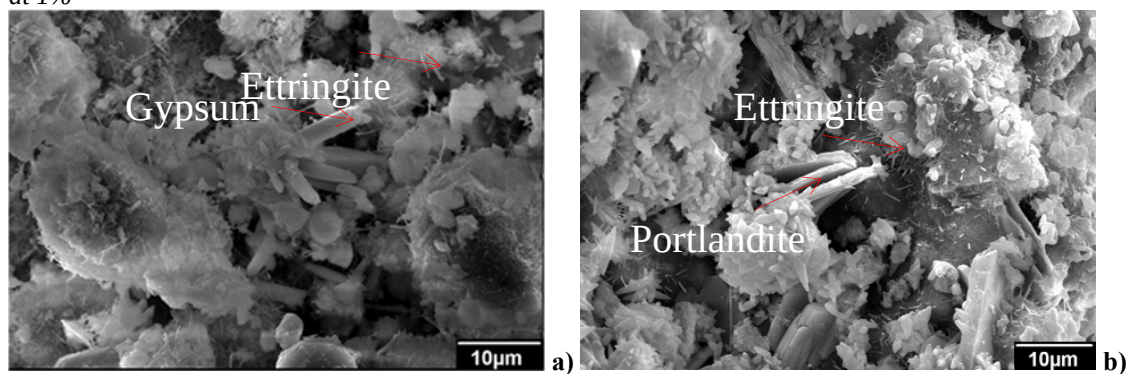


Fig. 5– SEM – Ettringite, and portlandite: a) 7 days - TP/OS/50/A/1/7, b) 28 days - TP/OS/50/A/1/28

Preferable Use of Hybrid Cement in Concrete Intended for Industrial Applications

I. Janotka, P. Martauz and Michal Bačuvčík

Synopsis: Important properties of the novel hybrid cement, H-Cement, are due to the use of fly ash, metallurgical slag, alkaline waste water from red mud deposits and ordinary portland clinker. H-Cement saves around 80 % of CO₂ emissions compared to ordinary portland cement (OPC) production and enables effective recovery and safe disposal of industrial wastes. H-Cement is suitable for the preparation of ready-mixed concretes of strength classes between C8/10 (1160/1450 psi) and C30/37 (4350/5370 psi) and as a shrinkage-reducing and alkali-silica reaction (ASR)-mitigation agent. This cement provides a slight expansion-reducing effect in permanent water curing at 20 °C (68 °F) and an evident shrinkage-reducing effect in permanent dry curing at 20 °C (68 °F) / 60 % R. H. and 40 °C (104 °F) / 15 % R. H. -air relative to OPC. The ASR is suppressed at 20 °C (68 °F) and 40 °C (104 °F) / 100 % R. H. -air cure.

Keywords: alkali-silica reaction, concrete, hybrid cement; strength, shrinkage,

INTRODUCTION

Global annual production of cement accounts to about 5 % of the total anthropogenic CO₂ emission [1]. About 4.2 GJ energy is required to produce 1 metric ton (1.102 US short ton) of OPC, resulting in approximately 0.8 - 1.0 metric ton (0.9 - 1.1 US short ton) of CO₂ release into the atmosphere [2]. A second problem besides CO₂ emissions is connected with the negative ecological and health impact of red and brown mud ponds in the manufacture of aluminum containing high alkaline waste water rich in NaOH. Landfilling of this hazardous waste raises other problems due to the high concentrations of heavy metals and the variety in chemical composition depending to a large extent on the season and weather conditions. The main task of the research is the development of less energy intensive but more ecological cements. One solution is the production of innovative cement binders like alkali-activated cements - geopolymers and hybrid alkaline cements with portland clinker addition [3, 4]. The hybrid alkaline cements have various compositions of alkali-activated aluminosilicates with low portland clinker content [5]. In spite of the low clinker content, the hybrid binders can obtain useful early age mechanical strengths [6]. Hybrid cements take advantage of the material properties of a cement and ordinary geopolymer with the resulting benefit on acquired properties, so that hybrid cement can replace in large quantities energy-intensive OPC [7]. The novel hybrid cement, H-Cement, is produced on the base of industrial by-products and wastes according to a patent application [8]. The content of clinker is always under 30 % wt. Typical feature for H-Cement binding phase formation is the combined effect of hydraulic properties of portland clinker, pozzolanic properties of fly ashes, latent hydraulic properties of granulated blast-furnace slag (GBFS) and geopolymeric properties coming from the alkaline inorganic polycondensing reactions of alumino-silicate materials. The geopolymers are activated by addition of alkaline waste water separated from the caustic red mud ponds and Na₂SO₄ obtained from alkaline waste water neutralization by H₂SO₄. In the presence of these alkaline agents, the pH value of cement mixture is increased. This results in fly ash and GBFS dissolution leading to geopolymerization. At the same time, Ca(OH)₂ addition originating from portland clinker hydration promotes the binding reactions of fly ash and GBFS. H-Cement is characterized by lower early strength and lower hydration heat but higher long-term strengths. H-Cement possesses high chemical resistance against aggressive action of sulfate, magnesium, chloride and acidic waters [9]. The production of H-Cement does not require additional heat treatment. It is treated the same way as traditional cements, and owns the Certificate of conformity [10] issued on the base of SK Technical Assessment [11]. H-Cement is special green cement which, due to its material composition, does not suit the categorization of cements according to STN EN 197-1 [12].

This paper shows the basic properties of H-Cement prepared with maximal content of wastes and by-products and only 20 % wt. of Portland clinker. The applicability of H-Cement in ready-mixed concrete with special emphasis on use of suitable superplasticizers for improving fresh concrete workability is presented. Shrinkage-reducing and alkali-silica reaction (ASR)-mitigating property of H-Cement are confirmed as well.

RESEARCH SIGNIFICANCE

One possible solution for innovative binders with improved durability and decreased energy requirements is the production of hybrid cements. Hybrid cements consist as far as possible of reduced portland clinker and extended waste contents, and require suitable alkaline activators developed for this purpose. The shrinkage-reducing and ASR-mitigating character of H-Cement is especially relevant because it prevents propagation of shrinkage or expansion cracking during the service life of the concrete.

EXPERIMENTAL PROCEDURE

Materials and Methods

The novel H-Cement and CEM I/42.5 R (6525 psi) (OPC) as a reference were tested. Both are produced by cement plant Považská cementáreň, Ladce in Slovakia according to STN EN 197-1. The chemical composition of H-Cement and its solid and liquid constituents are listed in Tables 1 and 2, respectively. The cement was used in combination with river aggregates of 0/4, 4/8 and 8/16 mm (0/0.15, 0.15/0.315 and 0.315/0.630 in) fraction from Jelka, (Slovakia). All aggregate properties met the requirements of STN EN 12620 + A1 [13]. The compatibility of H-Cement was verified with seven types of plasticizers. The concrete without admixture was examined as a reference. The shrinkage-reducing ability was confirmed on the concrete made from H-Cement, OPC and selected mixed systems. The H-Cement suitability for mitigating alkali-silica reaction was verified on the cement mortars by the procedure reported in STN 72 1179 [14] (the related ASTM Standards: C289 – 03 for Chemical method; ASTM C1293 – 08b for length change of concrete).

Casting

Specimens of ready-mixed concrete were made according to STN EN 12390-2 [15]. Fresh concrete was compacted on a vibration table (40 Hz) for 60 seconds and cast into 150 mm (6 in) cubes or (100 100 400)

mm (4 × 4 × 16 in) prisms. Casting of the specimens for verification of special properties of H-Cement is reported separately for each.

Curing

The molds were stored at more than 95 % relative humidity (abbreviated as R. H.) at (20 ± 1) °C (68 ± 3 °F) for the first 24 hours and then the concrete specimens were cured according to the test until testing. A method of treating the specimens is given separately for each test.

Testing procedures for cement

Both cements were tested for chemical composition by STN EN 196-2 [16]; the Bogue mineral composition as shown in Table 3 was also determined. Standard consistency, initial and final setting and soundness were verified by STN EN 196-3 + A1 [17], and hydration heat by STN EN 196-8 [18]. After 2-, 28- or 90- day cure, flexural and compressive strengths of the mortars with cement to sand ratio 1 : 3 by weight were obtained according to STN EN 196-1 [19]. H-Cement is sensitive to excess of water; the OPC and H-Cement mortars therefore differ in water - to - cement ratios. The comparison of important qualitative parameters of both cements is reported in Table 4.

Testing procedure for fresh and hardened concrete

The consistency of fresh concrete was estimated by slump (STN EN 12350-2), volume density by STN EN 12350-6 and air content in the fresh mixture by STN EN 12350-7 [20 - 22]. Concrete specimens were tested for cube compressive strengths [23], compressive strengths of the edges of prisms of standard size [24] and dynamic elasticity modulus [25] (the related ASTM Standard: C597 – 16).

EXPERIMENTAL RESULTS AND DISCUSSION

Basic characterization of H-Cement

H-Cement with obviously different chemical and mineral composition relative to those of OPC shows different typical characteristic values in comparison with OPC (Tables 1 to 4). Taking into account the economic (the lower price) and environmental benefits of H-Cement (the reduction of CO₂ emissions and disposal of red mud waste) compared to OPC, the results suggest that hybrid cement can be used prospectively in a normal-strength concrete for the same purposes as the blended cements of lower strength classes e.g. CEM III to V, probably CEM II/B-S according to STN EN 197-1, preferably in massive constructions due to low hydration heat and aggressively exposed media because of low portland clinker (C₃A) content. The latter assumption is supported by yet unpublished 5-year findings from the verification of sulfate resistance of H-Cement mortar compared to those made with OPC and sulfate-resistant cement with zero C₃A content; this test will be completed in August 2017 after 5-year exposure in 5 % Na₂SO₄ solution.

Ready-mixed concrete

The compositions of ready-mixed concretes of C8/10 (8/10 MPa on cylinders/cubes; 1160/1450 psi) and C30/37 (4350/5370 psi) strength class for reaching a slump of 100 - 150 mm (4 - 6 in) (slump class S3 according to [26]) without use of plasticizers and cube compressive strengths $f_{ck,cube}$ after 2-, 7- and 28-days of water curing are given in Table 5. The mixture composition of ready-mixed concretes prepared with different plasticizers with a slump ≥ 220 mm (≥ 8.5 in) [slump class S5 according to (26)] is reported in Table 6. The consistency of fresh mixtures and those after a 60 minute standing time, and cube compressive strengths are listed in Table 7. Laboratory-made ready-mixed concrete specimens were prepared with the following types of plasticizers coming from various producers: M1 – no admixture, M2 – lignosulfonate, M3 - modified polycarboxylate (less than 22 % polycarboxylate content), M4 – polycarboxylate (30 % water reducing effect), M5 – modified polycarboxylate (more than 22 % polycarboxylate content), M6 – polycarboxylate (35 % water reducing effect), M7 – melamine, M8 – lignosulfonate modified by polycarboxylate.

The results show that H-Cement is suitable for the production of ready-mixed concretes between C8/10 (1160/1450 psi) to C30/37 (4350/5370 psi) strength classes. Workability of the concretes made from H-Cement is dependent on the specific plasticizer type being used. Admixtures based on a lignosulfonate and a combined lignosulfonate/polycarboxylate mixture are found as the best to ensure the workability of fresh concrete mixtures and also after the 60 minutes standing time.

Shrinkage-reducing property

The concretes were prepared from the cement mixture made of two cements, H-Cement and OPC in the selected ratios (expressed as % wt.) as seen in Table 8. The specimens were stored in water at 20 ± 1 °C (68 ± 3 °F) (indicated as W20), in air at 20 ± 1 °C (68 ± 3 °F) with 60 % R. H. (A20), and in air at 40 ± 1 °C (104 ± 3 °F) (A40) with an average R. H. of 15 % in order to minimize the volume changes within the 90-day period of

curing. The concretes were prepared with a constant water - to - cement ratio of 0.475 according to the proportion: 400 kg/m³ (758 lb/yd³) of cement or cement mixture, 190 liters (55.9 gal) of water and dried Jelka aggregates: 0/4 mm (0/0.157 in) - 630 kg (1389 lb), 4/8 mm (0.157/0.315 in) - 390 kg (860 lb) and 8/16 mm (0.315/0.630 in) - 775 kg (1708 lb). No admixture was used at the concrete production to preclude its influence on the measurement of volume changes. In water the expected expansion of OPC was corrected by small H-Cement addition (between 5 - 15 % wt.) to the cement mixture (Table 8: PCH 0.95, PCH 0.90 and PCH 0.85). On the contrary, for dry curing it was necessary to reduce the apparent shrinkage of OPC by higher addition of H-Cement (between 85 - 95 % wt.), which gave a lower shrinkage of the cement mixture over time (Table 8: HPC 0.85, HPC 0.90 and HPC 0.95). The ratio of 50 % wt. H-Cement to 50 % wt. OPC (indicated as HPC 0.50) represents the mean value between two marginal systems [100 % wt. H-Cement (HPC 1.00) and 100 % wt. OPC (PCH 1.00)], which were exposed to all treatment regimes. The volume changes were measured on prisms (100 100 400) mm (4 × 4 × 16 in) having a length comparator according to STN 73 1320 [27] (the related ASTM Standard: C157/C157M – 08).

Fresh concrete properties and 2-day compressive strengths of two marginal composition mixtures (HPC 1.00 and PCH 1.00) are listed in Table 9. Mechanical properties of all concrete types are reported in Table 10. The length changes measured in water and both dry air - cure regimes are illustrated in Figures 1 to 3. Table 11 compares the length change data and provides evidence of the shrinkage-reducing property of H-Cement.

The results show that H-Cement has reduced shrinkage. All concretes expand when permanently cured in water; however, H-Cement demonstrates a minor expansion-reducing effect. H-concrete expands by 21.6 % less than P-concrete after 90-days in water. The shrinkage of H-concrete exposed for 90 days in 20 °C (68 °F) / 60 % R. H. -air and 40 °C (104 °F) / 15 % R. H. -air is about 48 % and 58 % smaller than that of P-concrete. The shrinkage-reducing effect is also recorded by the blended systems depending on its cement blend composition and curing regime.

ASR-mitigating property

The ground andesite aggregate with a proven susceptibility to ASR was sieved through a 0.063 mm (230) mesh to obtain the powder applicable for testing of mineral composition (Philips XRD diffractometer running in a 2 θ range of 2 - 65°, CuK radiation and Ni-filter). The patterns show albite and anorthite belonging to the group of feldspar minerals with quartz as dominant minerals and cristoballite as one SiO₂ modification as a minor constituent, present in the andesite (Fig. 4). The XRD high background within 2 - 60° 2 θ range indicates the presence of an amorphous phase, which is likely a volcanic glass and mainly responsible for susceptibility to ASR. Criteria for evaluation of the chemical test according to STN 72 1179 (14) are listed in Table 12. Prediction of andesite aggregate susceptibility to ASR by the results of the chemical test is given in Table 13. The composition of mortars for 6-month length change test cured at 20 °C (68 °F) and 40 °C (104 °F)/100 % R. H. -moist air is reported in Table 14. The results show that H-Cement is characterized by ASR-mitigating property (Fig. 5). H-Cement, in contrast with OPC, clearly reduces the expansion markedly below the maximum allowable limit of 0.1 % (1 ‰) regardless of the long-term treatment. ASR-mitigating effect under maximum allowable limit of 0.1 % (1 ‰) is confirmed also for the blended cement with 70 % wt. OPC and 30 % wt. H-Cement (abbreviated as HM 20 and HM 40 in Fig. 5).

CONCLUSIONS

The following options for hybrid cement application in practice have been demonstrated by the research carried out to this day:

- H-Cement with 20 % wt. of portland clinker and 80 % wt. of alkali-activated inorganic polymer can be used similarly to traditional cements; no kind of additional heat treatment during early and later hydration is needed.
- H-Cement is suitable for use in ready-mixed concrete up to C30/37 (4350/5370 psi) strength class with a variety of plasticizers, which are compatible with it in the same way as traditional cements. Lignosulfonate-based and combined lignosulfonate-polycarboxylate plasticizers have found to be the best in terms of workability of fresh mixtures standing for 60 minutes.
- H-Cement has under the conditions tested shrinkage-reducing properties. Shrinkage-reducing effect is also recorded in cement blends at replacement level of H-Cement by 5 to 15 % wt. OPC. No shrinkage-reducing admixture is necessary in concrete, when H-Cement is used.
- H-Cement has under the conditions tested ASR-mitigating property. The expansion of concrete is also suppressed when using cement blend with replacement level of OPC by 30 % wt. H-Cement.

Current attention is given to the investigation of early and long-term strengths and the proof of frost resistance of concretes that meet standardized requirements. Standardization of non-standard hybrid cement is a key step to faster market applications.

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[25] STN 73 1371: 1981 Method of ultrasonic pulse testing of concrete.

[26] STN EN 206: 2015 Concrete. Specification, performance, production and conformity

[27] STN 73 1320: 1987 Determination of volume changes of concrete.

Table 1 – Chemical composition of H-Cement (as HC) and its main solid components

% wt.	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Na ₂ O	L.O.I.
H-Cement	22.55	43.55	17.52	5.86	2.68	3.85	2.74	2.49	1.51
OPC clinker	66.13	21.69	5.31	2.83	1.44	0.53	1.00	0.04	0.85
GBFS	39.24	40.13	7.19	0.27	10.04	1.50	0.52	0.31	1.10
Fly Ash	3.36	51.42	26.93	7.27	2.10	0.87	3.28	0.17	1.84

Notice: L.O.I. means loss on ignition

Table 2 – Chemical composition of highly alkaline waste water from red mud pond as standard water from the pond (Standard) and concentrate water from the evaporator (Concentrate)

Waste water	mg/l ($\times 10^{-5}$ lb/gal)								pH
	Ca	Si	Al	Fe	Mg	Na	K	(SO ₄) ²⁻	
Standard	6.9 (5.7)	59.8 (49.9)	538 (448.9)	0.64 (0.5)	1.9 (1.6)	11820 (9864.3)	156 (130.2)	4072 (3398.3)	13
Concentrate	12.5 (10.4)	189 (158)	2143 (1788)	26.0 (21.7)	4.4 (3.7)	53990 (45057)	710 (592.5)	24098 (20111)	13

Table 3 – Mineral composition of H-Cement (HC) and OPC

% wt.	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	C _{free}	MgO	SiO ₂	K ₂ SO ₄	Ca(OH) ₂	CaSO ₄
HC	13.28	2.49	1.95	1.59	0.30	0.07	0.02	0.20	0.11	-
OPC	61.50	10.3	6.93	10.71	0.26	0.35	0.28	1.63	1.23	8.66

Table 4 – Comparison of characteristic values of H-Cement and reference OPC

Technical parameters	Unit	H-Cement	OPC
Initial setting time	minute	200 ± 20	190 ± 20
Final setting time	minute	300 ± 40	250 ± 30
Standard consistency	%	32 ± 2.0	29.1 ± 1.8
2-day compressive strength	MPa (psi)	17.5 ± 3.0, w/c=0.4 (2540 ± 435)	33.7 ± 2.0, w/c = 0.5 (4890 ± 290)
28-day compressive strength	MPa (psi)	36.5 ± 4.0, w/c = 0.4 (5290 ± 580)	59.2 ± 1.6, w/c = 0.5 (8590 ± 230)
90-day compressive strength	MPa (psi)	41.5 ± 3.0, w/c = 0.4 (6020 ± 435)	63.1 ± 1.9, w/c = 0.5 (9150 ± 275)
2-day flexural strength	MPa (psi)	3.5 ± 0.5, w/c = 0.4 (510 ± 70)	6.4 ± 0.4, w/c = 0.5 (930 ± 60)
28-day flexural strength	MPa (psi)	4.4 ± 0.4, w/c = 0.4 (640 ± 60)	8.9 ± 0.4, w/c = 0.5 (1290 ± 60)
90-day flexural strength	MPa (psi)	9.0 ± 0.3, w/c = 0.4 (1300 ± 40)	9.3 ± 0.3, w/c=0.5 (1350 ± 40)
Le Chatelier	mm (in)	0.5 (0.0197)	0.01 (0.0004)
Content of Cr ^{VI}	(ppm)	1.0	1.23
Content of C ₃ A	% wt.	2.0 ± 0.5	7.5 ± 0.8
Hydration heat	J/g (cal/g)	185 (44.2)	359 (85.7)

too plastic consistency at w/c = 0.5

Table 5 – Ready - mixed concrete compositions with H-Cement (HC) at the same slump S3

Concrete strength class	HC	Water	Aggregates, kg (lb)			Strengths $f_{ck,cube}$, MPa (psi)		
	kg/m ³ (lb/yd ³)	kg/m ³ (lb/yd ³)	0/4, mm (0/ 0.16 in)	4/8, mm (0.16/ 0.32 in)	8/16, mm (0.32/ 0.63 in)	2, days	7, days	28, days
C8/10	270 (595)	185 (408)	762 (1680)	362 (798)	781 (1722)	4.8 (690)	10.4 (1510)	16.0 (2320)
C12/15	300 (661)	190 (419)	707 (1559)	372 (820)	781 (1722)	5.7 (830)	11.4 (1650)	18.7 (2710)
C16/20	360 (794)	190 (419)	627 (1382)	376 (829)	788 (1737)	6.9 (1000)	14.6 (2120)	22.2 (3220)
C20/25	400 (882)	190 (419)	592 (1305)	361 (796)	773 (1704)	8.0 (1160)	16.8 (1510)	25.0 (3630)
C30/37	350 (772)	147 (324)	602 (1327)	565 (1246)	657 (1448)	14.6 (2120)	29.4 (4260)	42.6 (6180)

Table 6 – Composition of fresh C20/25 ready-mixed concretes with different kinds of plasticizers with the same slump S5

Concrete strength class C20/25	H-Cement, kg/m ³ (lb/yd ³)	Water, kg/m ³ (lb/yd ³)	Plasticizer, kg/m ³ (lb/yd ³)	Aggregates, kg (lb)		
				0/4, mm (0/ 0.16 in)	4/8, mm (0.16/ 0.32 in)	8/16, mm (0.32/ 0.63 in)
M1	400 (882)	220 (485)	-	753 (1660)	263 (580)	735 (1620)
M2	400 (882)	212 (467)	3.0 (6.6)	753 (1660)	263 (580)	735 (1620)
M3	400 (882)	217 (478)	2.0 (4.4)	753 (1660)	263 (580)	735 (1620)
M4	400 (882)	217 (478)	2.0 (4.4)	753 (1660)	263 (580)	735 (1620)
M5	400 (882)	215 (474)	2.0 (4.4)	753 (1660)	263 (580)	735 (1620)
M6	400 (882)	201 (443)	2.0 (4.4)	753 (1660)	263 (580)	735 (1620)
M7	400 (882)	216 (476)	3.0 (6.6)	753 (1660)	263 (580)	735 (1620)
M8	400 (882)	228 (503)	3.0 (6.6)	753 (1660)	263 (580)	735 (1620)

Notice: Plasticizers (abbreviated as M2 to M8) used for concrete manufacture are described in text relevant to Tables 6 and 7.

Table 7 – Properties of fresh ready-mixed concrete mixtures with different kinds of plasticizers and the cube compressive strengths $f_{ck,cube}$ after 2, 28, 56 and 90 days

Concrete strength class C20/25	Entrapped air	Slump		Cube compressive strengths, $f_{ck,cube}$, MPa (psi)			
	after mixing, % vol.	after mixing, mm (in)	after 60 minutes, mm (in)	2, days	28, days	56, days	90, days
M1	1.2	220 (8.7)	120 (4.7)	11.0 (1590)	23.6 (3420)	24.8 (3600)	26.3 (3810)
M2	2.1	220 (8.7)	130 (5.1)	11.0 (1590)	25.0 (3620)	27.1 (3930)	28.4 (4120)
M3	1.7	220 (8.7)	60 (2.4)	10.6 (1540)	21.8 (3160)	22.5 (3260)	22.6 (3280)
M4	1.6	220 (8.7)	70 (2.8)	9.3 (1350)	21.2 (3075)	22.5 (3260)	22.7 (3290)
M5	1.7	220 (8.7)	110 (4.3)	10.1 (1465)	23.6 (3420)	26.6 (3860)	25.4 (3680)
M6	1.4	220 (8.7)	170 (6.7)	8.6 (1250)	22.6 (3280)	24.1 (3490)	23.7 (3440)
M7	2.3	220 (8.7)	40 (1.6)	7.1 (1030)	24.0 (3480)	24.6 (3570)	29.9 (4340)
M8	1.3	220 (8.7)	190 (7.5)	9.4 (1360)	22.2 (3220)	21.1 (3060)	24.6 (3570)

Table 8 – Content of cements in the concrete mixtures with w/c = 0.475

Cement mixture in concrete	Content of cements, % wt.		Curing regime
	HC	OPC	
PCH 1.00	0	100	in water at 20 °C (68 °F) and in air at 20 °C (68 °F) and 40 °C (104 °F)
PCH 0.95	5	95	
PCH 0.90	10	90	
PCH 0.85	15	85	
HPC 0.50	50	50	in water at 20 °C (68 °F) and in air at 20 °C (68 °F) and 40 °C (104 °F)
HPC 0.85	85	15	
HPC 0.90	90	10	
HPC 0.95	95	5	
HPC 1.00	100	0	in water at 20 °C (68 °F) and in air at 20 °C (68 °F) and 40 °C (104 °F)

Table 9 – Rheological properties, volume density and 2-day strength of two concrete mixtures

Fresh concrete	Consistency, mm (in)	Volume density, kg/m ³ (lb/yd ³)	Air content, % vol.	2-day compressive strength, MPa (psi)
HPC 1.00	10.5 (0.41)	2380 (4012)	1.3	10.1 (1465)
PCH 1.00	6.0 (0.24)	2420 (4079)	1.1	19.3 (2800)

Table 10 – Mechanical properties of the concretes made from a mixture of H-Cement and OPC stored for 90 days in water at 20 °C (68 °F) (W20), in air at 20 °C (68 °F)/60 % R. H. (A20) and at 40 °C (104 °F) /15 % R. H. (A40) after 28-days basic curing

Concrete mixture	H-cement content, % wt.	Curing conditions	28-days basic curing	90-days curing		
			Compressive strength, MPa (psi)	Dynamic modulus of elasticity, GPa (ksi)	Strength at the ends of prisms, MPa (psi)	
					flexural	compressive
HPC 1.00	100	W20	27.2 (3945)	46.6 (6760)	5.4 (785)	34.2 (4960)
		A20	27.6 (4000)	41.7 (6050)	2.4 (350)	32.3 (4685)
		A40	28.7 (4160)	36.7 (5325)	2.3 (335)	30.6 (4440)
HPC 0.95	95	A20	29.3 (4250)	41.4 (6005)	2.8 (405)	32.9 (4770)
		A40	30.0 (4350)	36.7 (5325)	2.4 (350)	31.8 (4610)
HPC 0.90	90	A20	31.3 (4540)	41.3 (5990)	2.9 (420)	34.8 (5045)
		A40	32.0 (4640)	36.6 (5310)	2.5 (365)	33.0 (4785)
HPC 0.85	85	A20	32.4 (4700)	41.4 (6005)	3.0 (435)	37.2 (5395)
		A40	33.2 (4815)	36.6 (5310)	2.6 (375)	34.7 (5035)
HPC 0.50	50	W20	35.7 (5180)	50.3 (7295)	5.5 (800)	49.1 (7120)
		A20	38.1 (5525)	41.2 (5975)	3.3 (480)	41.0 (5945)
		A40	38.5 (5585)	36.5 (5295)	3.2 (465)	38.5 (5585)
PCH 0.85	15	W20	40.5 (5875)	55.1 (7990)	5.5 (800)	50.6 (7340)
PCH 0.90	10	W20	40.5 (5875)	55.9 (8110)	5.5 (800)	50.7 (7355)
PCH 0.95	5	W20	41.0 (5950)	56.6 (8210)	5.5 (800)	51.4 (7455)
PCH 1.00	0	W20	41.6 (6035)	56.6 (8210)	5.6 (810)	54.5 (7905)
		A20	40.2 (5830)	39.3 (5700)	3.7 (535)	42.0 (6090)
		A40	39.1 (5670)	33.4 (4845)	3.8 (550)	39.0 (5655)

Notice: Basic curing (abbreviated as BC) is specified by 1- day cure in the chamber at (20 ± 1) °C (68 ± 3 °F) at 100 % R. H.-air and 27- days curing in water at (20 ± 1) °C (68 ± 3 °F).

Table 11 – Comparison of the level of expansion in H-concrete and P-concrete after 90 days of curing in water at 20 °C (68 °F) (W20) and the level of shrinkage in H-concrete and P-concrete after 90 days of curing in air at 20 °C (68 °F) / 60 % RH (A20) and 40 °C (104 °F) /15 % RH (A40)

Concrete and curing	Level of concrete expansion after 90 days of curing, ‰*	Difference in concretes expansion, ‰	Expansion reduction of H-concrete opposite to P-concrete, % vol.
H-concrete W20	0.080	0.022	21.6
P-concrete W20	0.102		
Concrete and curing	Level of concrete shrinkage after 90 days of curing, ‰	Difference in concretes shrinkage, ‰	Shrinkage reduction of H-concrete relative to P-concrete, vol. %
H-concrete A20	-0.211	0.195	48.0
P-concrete A20	-0.406		
H-concrete A40	-0.152	0.213	58.4
P-concrete A40	-0.365		

*1 ‰ = 1/1000 % (related also to Figures 1 – 3 and 5)

Table 12 – Criteria for evaluation of chemical test to ASR

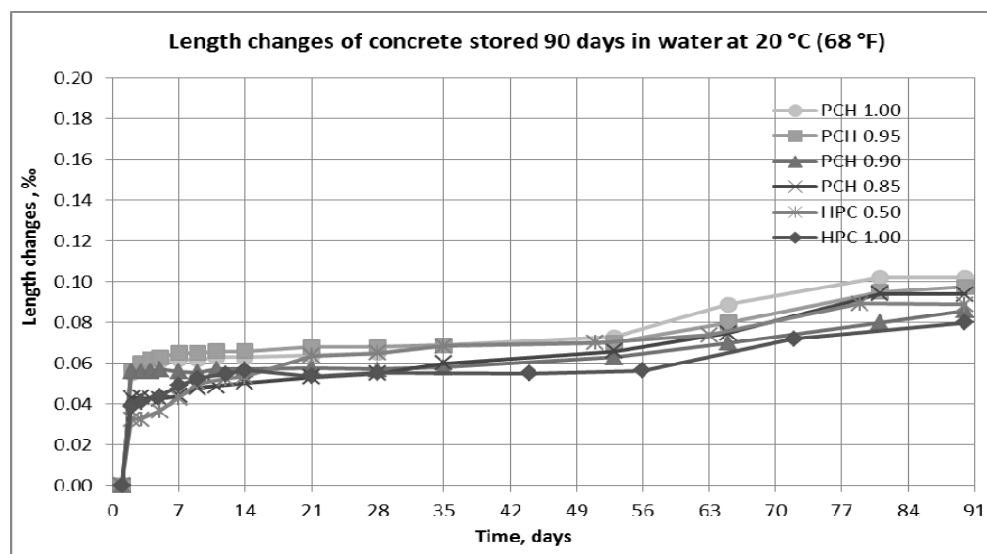
Chemical test according to STN 72 1179 (14)	Unit	The criterion for aggregate, which is free of reactive forms of SiO ₂
Molar concentration of SiO ₂ S	mmol/l (gr/gal)	a) if R > 70 (409), so they must be S < R
Loss of alkalinity R		or b) if R < 70 (409), so they must be S < 35 (205) + R/2

Table 13 – Prediction of andesite susceptibility to ASR by the chemical test

Aggregate	Loss of alkalinity R, mmol/l (gr/gal)	Molar concentration of SiO ₂ S, mmol/l (gr/gal)	R value according to criteria in the Standard (14)	S value according to criteria in the Standard (14)	Assumption that aggregate contains reactive forms of SiO ₂
Andesite	132.42 (774.24)	400.04 (2338.98)	R > 70 (409)	S > R	YES

Table 14 – Composition of mortars for length change test according to STN 72 1179

Denotation of mortar	Component contents, g (lb)			
	CEM I	H-Cement	water	aggregate
PC – 100 % wt. OPC and andesite aggregate	600 (1,32)	-	300 (0,66)	1200 (2,65)
HC – 100 % wt. H-Cement and andesite aggregate	-	600 (1,32)	300 (0,66)	1200 (2,65)
HM – 70 % wt. OPC/30 % wt. H-Cement and andesite aggregate	420 (0,93)	180 (0,40)	300 (0,66)	1200 (2,65)

**Figure 1** — Length changes of concretes stored 90 days in water at 20 °C (68 °F)

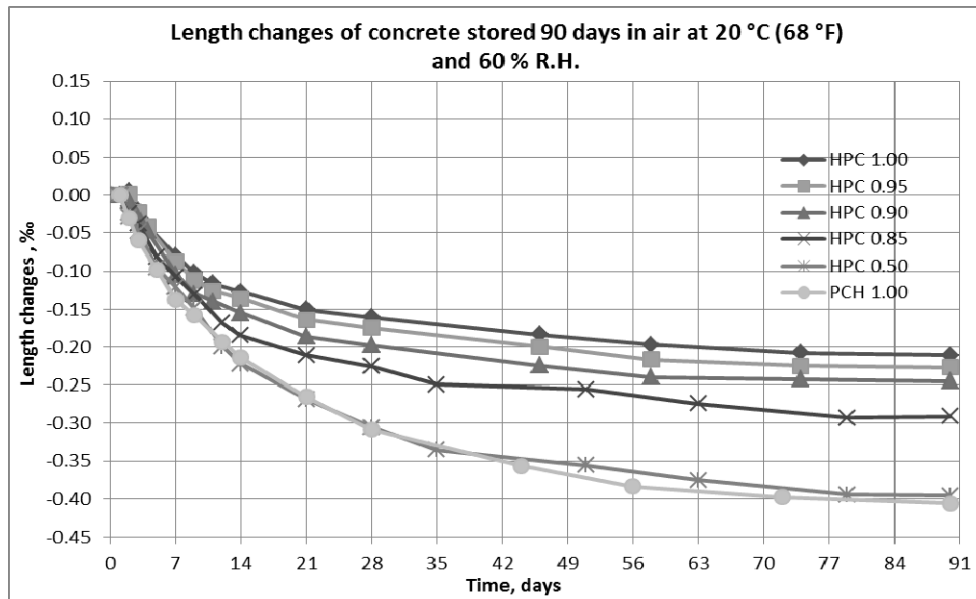


Figure 2 — Length changes of concrete stored 90 days in air at 20 °C (68 °F) / 60 % R. H.

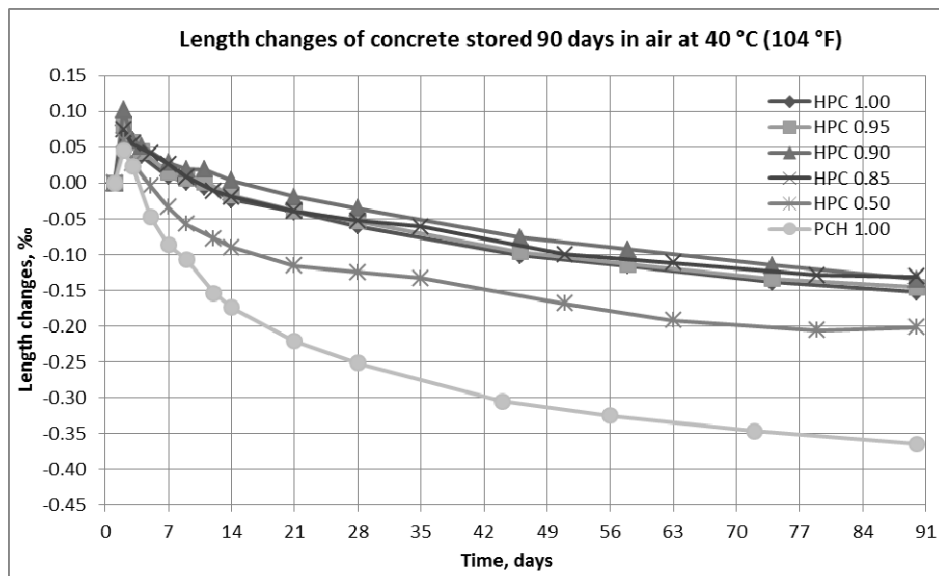


Figure 3 — Length changes of concrete stored 90 days in air at 40 °C (104 °F) / 15 % R. H.

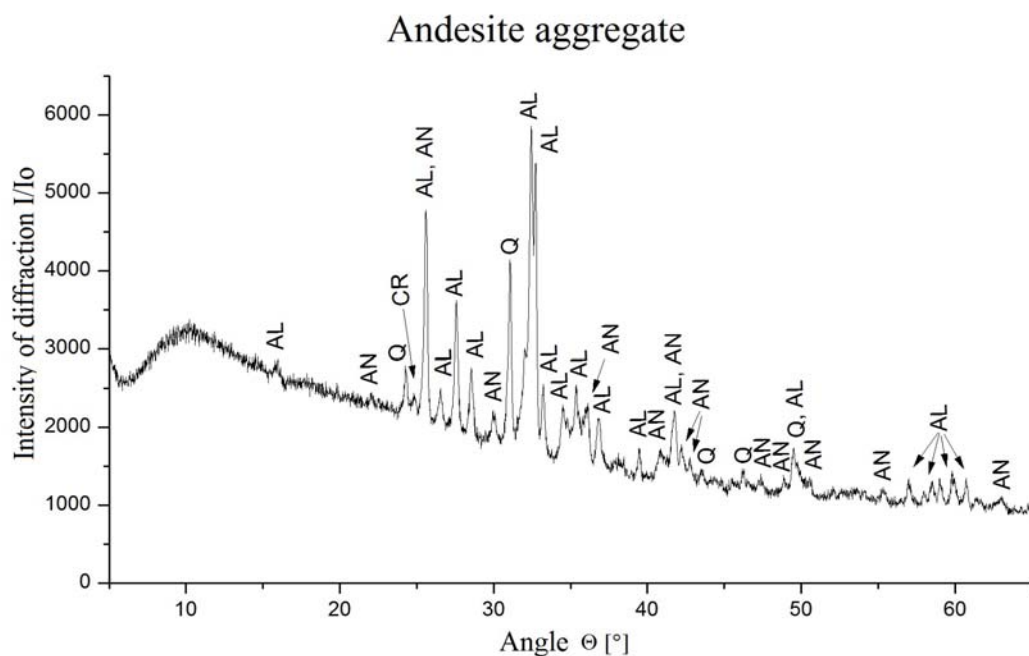


Figure 4 — Mineral composition of andesite aggregate

Abbreviations: Q – quartz SiO_2 , AL – albite $(\text{Na,Ca})\text{Al}(\text{Si,Al})_3\text{O}_8$ (mineral belonging to the group of Na-Ca feldspars), AN – anorthite $\text{CaAl}_2(\text{SiO}_4)_2\text{CaO} \cdot 2\text{SiO}_2$ (mineral belonging to the group of Ca-Al feldspars), CR – cristoballite as one of modification forms of SiO_2

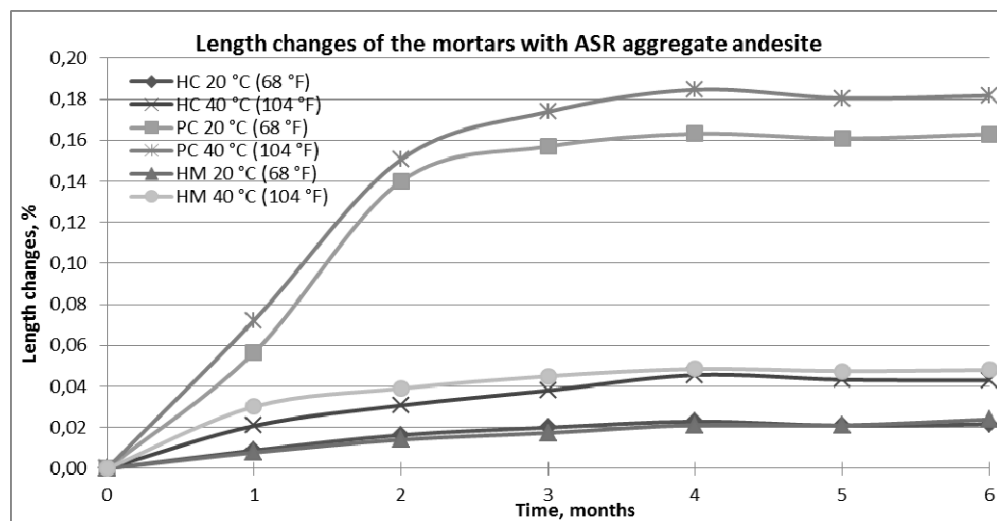


Figure 5 — Length change of the mortars cured in 20 °C (68 °F) and 40 °C (104 °F) /100 % R. H. - moist air for 6 months

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Low-Energy Alinite Cement from Soda Sludge Waste

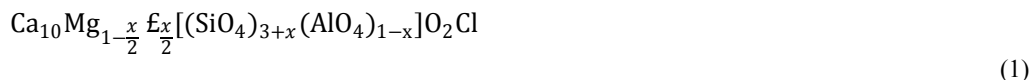
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Synopsis: Alinite cement which was developed in 1970s is an alternative inorganic, low-energy binding material in which chlorine containing wastes can be utilized. Although potentially a suitable candidate, there is little research on utilization of soda sludge waste in cementitious systems. In this experimental study, synthesis and optimization of the properties of alinite cement by using soda sludge waste as a raw material was carried out by investigating optimum calcination temperature and calcination duration, chemical and mineralogical compositions, and hydration products. When raw meal was calcined at 1150°C for 2 hours, the resulting clinker contained alinite, belite, and calcium aluminochloride phases with sufficiently low free calcium oxide and alkali content. Upon hydration of ground alinite cement clinker and gypsum mixture, peaks of portlandite, Friedel's salt-like phase, and calcium chloride silicate sulfate were distinguished in X-Ray diffractograms. Compressive strength tests of alinite cement mortars gave satisfactory results.

Keywords: alinite cement, low-energy cement, soda sludge waste, waste utilization

INTRODUCTION

Cement replacement materials have been a primary research area in cement and concrete technology for a long time. Use of industrial by-products in cementitious systems instead of disposal is important both environmentally and economically. On top of that, they are able to improve performance of concrete. Over the years, numerous conferences focusing on cement replacement materials and alternative binders have been held to contribute to sustainable cement and concrete production. Alinite cement is one of the proposed alternatives, which enables utilization of chlorine-containing wastes in cement production. It was developed and patented in the former Soviet Union by B. Noudelman. Alinite phase is the dominant phase in alinite cement clinker, instead of alite in portland cement clinker. Being a calcium oxy-chloro-aluminosilicate, alinite is related to alite (tricalcium silicate), with the difference that Ca^{2+} (and Mg^{2+}) cations are balanced by SiO_4^{4-} , AlO_4^{5-} , O^{2-} and Cl^- anions in alinite's structure unlike alite's, where Ca^{2+} cations are balanced by SiO_4^{4-} and O^{2-} anions¹. Although it has no definite composition, alinite can be expressed with the following formula:



where $0.35 < x < 0.45$ and E means a lattice vacancy².

The main advantage of alinite cement over normal portland cement is the lower energy requirement for production due to its lower clinkering temperature and easier grindability^{2,3,4}. It was also reported that alinite cement requires lower w/c than that of portland cement for the same consistency⁵. However, when water-soluble chloride is available in the pore solution, it creates the risk of corrosion of reinforcement steel in concrete^{6,7}. Although this availability is reported to be depended on factors such as raw meal composition⁶ and exposure conditions⁸, use of alinite cement in reinforced applications should be discouraged until its hydration behavior is fully understood.

Although suitability of different wastes had been investigated^{3,9,10,11}, research on the use of soda sludge waste as a raw material in cement production is limited. Soda sludge waste, which is mainly composed of calcium carbonate and calcium chloride, is the by-product of Solvay process used for soda ash production¹². Currently, the waste is discharged to rivers or settling ponds, which poses an environmental risk. As part of the effort to determine this waste's applicability within cementitious systems, alinite cement was produced from soda sludge waste in this study.

RESEARCH SIGNIFICANCE

Synthesizing alinite cement using different wastes as raw materials has been a topic of interest for decades^{3,9,10,11}. However, research on soda sludge waste as a raw material is very limited. In its dried form, soda sludge waste can be used as a calcium source in cement. Replacing limestone with soda sludge waste will result in less exploitation of natural resources as well as utilization of the waste. When composition of the waste and the positive environmental impact upon its possible utilization are considered, it was decided to determine the applicability of soda sludge waste in cementitious systems.

EXPERIMENTAL PROCEDURE

Raw mixture recipes were determined considering the chlorine-modified lime saturation factor (LSF_{mod}) and lime index (LI). In practice, lime saturation factor is used in portland cement production to estimate the ratio of alite to belite from raw meal composition. LSF_{mod} formula proposed for alinite cement clinker production by Ftikos et al.⁶ as:

$$\text{LSF}_{\text{mod}} = \frac{100x(\% \text{CaO} - 0.789\% \text{Cl})}{2.80\% \text{SiO}_2 + 1.18\% \text{Al}_2\text{O}_3 + 0.65\% \text{Fe}_2\text{O}_3} \quad (2)$$

It was stated that this value should be below 80, otherwise clinker burnability is reduced and alinite formation is inhibited⁶.

LI, which is the ratio of calcium oxide to the sum of silica, alumina, and ferrite oxides in the mixture by weight can be shown as:

$$LI = \frac{\%CaO}{\%SiO_2 + \%Al_2O_3 + \%Fe_2O_3} \quad (3)$$

According to Pradip et al.³, LI should not be less than 1.5 for measurable strength, and strength results improve linearly up to 1.8.

When soda sludge waste is dried in its original form without any filtration process, the resulting chlorine content is too high (see Table 1). Therefore, some mixtures were prepared as partial replacement of limestone with soda sludge waste. Raw mixtures were kneaded into cylindrical rods of approximately 10 mm (0.39 in.) diameter by adding small amounts of water. They were then fed into a furnace on a refractory. From each mixture, clinkers were produced with different maximum burning temperatures. Suitable samples were then produced with different calcination durations (burning duration at maximum burning temperature). Chemical and mineralogical analyses of clinkers were made to determine compound compositions. The chosen clinker was produced in bigger quantities and ground to 5000 cm²/g Blaine fineness. Ground alinite cement clinker was mixed with 6% separately ground gypsum. Hydration of alinite cement pastes was stopped at specific ages to determine hydration products by x-ray powder diffraction (XRD). Compressive strength results were also determined.

Materials

Limestone, clay and iron ore were used to produce alinite cement clinker along with dried soda sludge waste (DSSW), which partially replaced limestone in the raw meal. Chemical compositions and density values of raw materials can be found in Table 1. Recipes of clinker raw mixtures along with calculated LSF_{mod} and LI values can be seen in Table 2. Alinite cement clinker and gypsum were separately ground to around 5000 cm²/g Blaine fineness.

Specimens

Three different raw mixtures were investigated. Soda sludge waste was used as the only calcium source in the first mixture (A1). The other two were 30% and 50% replacements of limestone with dried soda sludge waste by mass, respectively (A2 and A3). Raw meal rods in a production furnace can be seen in Fig. 1. Clinkers were ground in a laboratory ball mill and sieved through 150 µm (#100) sieve opening for XRD. Alinite cement paste was prepared with 6% gypsum content and 0.40 w/c. Mineral phases of hydrated alinite cement paste were determined by XRD, after hydration was stopped at specific ages. Preliminary trials following the ASTM C1437 procedure¹³ showed that alinite cement requires lower w/c than that of portland cement for the same consistency. Therefore, for compressive strength tests, mortars with one part of cement, three parts of CEN standard sand, and 0.4 part water were mixed and molded in 40 mm x 40 mm x 160 mm (1.57 in. x 1.57 in. x 6.30 in.) prisms.

Items of investigation

Effects of calcination temperature and calcination duration on the clinkering process of different mixtures were observed by evaluating chemical and mineralogical compositions of clinkers. 1050°C and 1150°C were selected as calcination temperatures, and 1, 2, and 4 hours were selected as calcination durations to be investigated. The selected clinker was mixed with gypsum, and hydration products of this cement paste at 2 hours, 6 hours, 2 days, and 28 days of hydration were determined by XRD. The average strength of four specimens was recorded for compressive strength values at 2, 7, and 28 days.

EXPERIMENTAL RESULTS AND DISCUSSION

Raw meal composition, calcination temperature and duration

Results of chemical analyses of A1, A2, A3 clinkers with 1050°C and 1150°C calcination temperatures and 1 hour of calcination duration are presented in Table 3. It was clear that A1 recipe failed to produce a suitable mixture. Most of its raw meal melted, leaving only a small portion available for chemical analysis; and that portion contained a high content of alkali oxides and low calcium oxide. Also, its chlorine content was very high, even for alinite cement clinker.

The 1150°C calcination temperature provided better results for all mixtures. Therefore, 2 hours and 4 hours of calcination durations were also investigated with 1150°C calcination temperature for the A2 and A3 mixtures. Resulting chemical compositions are shown in Table 4. As can be seen, increasing calcination duration provides better results in terms of reducing free calcium oxide and alkali oxides content; however, the improvement is not very significant after 2 hours. Loss on ignition (LOI) values of alinite cement clinkers were higher relative to portland cement clinker, partly due to evaporation of chlorine upon heating.

Among the two, the A3 mixture provides higher waste utilization but the A2 mixture is expected to provide higher performance. Both have reasonably low free calcium oxide, but the A2 mixture contains less alkali oxides and a more moderate chlorine content. Therefore, A2 clinker with 1150°C calcination temperature and 2 hours of calcination duration (A2.1150.2) was investigated further in this paper.

Mineral phases of clinker

Mineral phases of the A2.1150.2 clinker were determined by XRD. Resulting phases are shown in Fig. 2. Alinite phase $[\text{Ca}_{10}\text{Mg}_{0.8}[(\text{SiO}_4)_{3.4}(\text{AlO}_4)_{0.6}]\text{O}_2\text{Cl}]$ was the prominent phase in the clinker. There were also significant peaks of belite. High presence of these two phases indicated that the clinker possesses good hydraulic properties. Apart from alinite and belite, calcium aluminochloride and calcium chlorosilicate phases were also determined.

Hydration products

Identified phases during the hydration of alinite cement are shown in Fig. 2. Calcium hydroxide peaks were noticeable starting from 6 hours of hydration. This indicated that the principal hydration reaction, which results in formation of C-S-H gel and calcium hydroxide, took place in alinite cement hydration.

A calcium aluminochloride hydrate which resembles Friedel's salt was detected as early as after 2 hours of hydration. In this phase, calcium chloride was partially replaced by calcium hydroxide and calcium carbonate, and it is expressed by the general formula $[\text{C}_3\text{A} \cdot (1-x-y)\text{CaCl}_2 \cdot x\text{CaCO}_3 \cdot y\text{Ca}(\text{OH})_2 \cdot 10\text{H}_2\text{O}]^2$. Presence of this phase is important as it is the main binder of chlorine within hydrated alinite cement products.

The peak of calcium chlorosilicate $[\text{Ca}_3(\text{SiO}_4)\text{Cl}_2]$ around $31^\circ 2\theta$ intensified throughout hydration. This implies that a product with a similar peak was produced while calcium chlorosilicate was consumed. As in previous research about soda waste¹⁴, it is concluded that a calcium chloride silicate sulfate was produced upon reaction of calcium chlorosilicate and gypsum during hydration, which yields a similar peak.

The intensity of alinite and belite peaks decreased as hydration progressed, as expected. The rate of decrease was higher in the case of alinite. Its peaks reduced noticeably at 2 days, and almost disappeared at 28 days. Belite peaks, on the other hand, were prominent even at 28 days of hydration.

Compressive strength

Compressive strength of alinite cement mortars at 2, 7, and 28 days of age are shown in Table 5. It was seen that compressive strength values comparable to that of portland cement can be attained with alinite cement.

FURTHER RESEARCH

Soda sludge waste used in this study was in unprocessed form. In this state, the chlorine content of the waste was very high. This permitted the use of waste only as partial replacement of limestone. In current practice, this sludge is filtrated before disposal to get rid of excess chlorine. This filtrated form of the waste can be used to utilize soda waste as the only calcium source in production of alinite cement. Also, this study investigated production and hydration properties of alinite cement. Yet, durability characteristics of alinite cement mortar and alinite cement concrete require further investigation. Water-soluble chloride content should be determined, and durability against corrosion and physical salt attack should be evaluated.

CONCLUSIONS

In this experimental study, synthesis and optimization of the properties of alinite cement by using soda sludge waste as a raw material was investigated. It was concluded that:

1. Low-energy and low- CO_2 alinite cement clinker could be successfully synthesized using soda sludge waste as partial replacement of limestone. Although it can also be produced at 1050°C, clinkers produced at 1150°C yielded better results in terms of lower chlorine, alkalis, and free calcium oxide contents.
2. Chemical compositions were slightly improved as calcination duration increased. Since this improvement was trivial after 2 hours, 2 hours of calcination duration was found to be suitable.
3. Alinite, belite, calcium aluminochloride, and calcium chlorosilicate phases were observed in clinker X-Ray diffractograms.
4. Upon hydration of alinite cement, compressive strength results comparable to that of portland cement could be achieved.

- Portlandite peaks in hydrated samples indicated the occurrence of hydration reactions which form C-S-H gel along with calcium hydroxide. Peaks of a calcium aluminochloride hydrate that resembles Friedel's salt, were also observed.
- Necessary precautions should be taken to prevent corrosion of production equipment. Use of alinite cement products in reinforced applications should be discouraged until its hydration behavior is fully understood.

ACKNOWLEDGMENTS

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NOTATION:

A = Alinite $[\text{Ca}_{10}\text{Mg}_{0.8}[(\text{SiO}_4)_{3.4}(\text{AlO}_4)_{0.6}]\text{O}_2\text{Cl}]$

B = Belite $[\text{C}_2\text{S}]$

CAC = $\text{C}_{11}\text{A}_7\cdot\text{CaCl}_2$

CCS = $\text{Ca}_3(\text{SiO}_4)\text{Cl}_2$

CCSS = $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{Cl}_2$

DSSW = dried soda sludge waste

F = Friedel's salt-like phase $[\text{C}_3\text{A}\cdot(1-x-y)\text{CaCl}_2\cdot x\text{CaCO}_3\cdot y\text{Ca}(\text{OH})_2\cdot 10\text{H}_2\text{O}]$

P = $\text{Ca}(\text{OH})_2$

XRD = X-Ray powder diffraction

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Table 1 - Chemical compositions of raw materials

Composition	Limestone	Clay	Iron Ore	DSSW	Gypsum Rock
LOI, %	42.73	9.89	11.7	24.85	18.9
SiO_2 , %	1.97	56.91	23.09	8.23	8.36
Al_2O_3 , %	0.68	14.65	3.92	1.82	1.96

Fe ₂ O ₃ , %	0.23	6.22	55.42	1.11	1.09
CaO, %	53.24	5.19	1.25	30.74	30.34
MgO, %	1.07	2.45	1.07	0.49	0.5
SO ₃ , %	<0.01	0.01	0.24	2.48	37.74
Na ₂ O, %	0.09	0.84	0.2	3.8	0.06
K ₂ O, %	0.05	1.94	0.18	0.36	0.33
TiO ₂ , %	-	0.84	0.07	0.13	0.14
P ₂ O ₅ , %	-	0.1	0.02	0.03	0.03
Cr ₂ O ₃ , %	-	0.17	1.94	0.02	0.01
Mn ₂ O ₃ , %	-	0.15	0.18	0.04	0.03
Cl ⁻ , %	0.0064	0.0102	0.0226	24.92	-
Density, g/cm ³	2.72	2.59	3.26	2.40	2.41

Table 2 - Recipes of raw mixtures and resulting indices

Mixture	Limestone (%)	DSSW (%)	Clay (%)	Iron ore (%)	LSF _{mod}	LI
A1	0	76.91	22.28	0.80	15.87	0.93
A2	54.66	23.43	20.61	1.30	67.98	1.76
A3	39.04	39.04	20.61	1.30	51.11	1.50

Table 3 - Chemical analysis of clinkers with different calcination temperatures

Composition	A1. 1050.1	A1. 1150.1	A2. 1050.1	A2. 1150.1	A3. 1050.1	A3. 1150.1
LOI, (%)	5.51	5.26	2.78	1.16	2.29	1.53
SiO ₂ , %	18.00	19.09	20.36	21.19	19.63	20.23
Al ₂ O ₃ , %	5.00	5.04	5.04	5.20	4.98	5.07
Fe ₂ O ₃ , %	2.45	2.53	3.02	3.24	2.78	3.06
CaO, %	40.55	40.90	57.80	60.38	53.00	53.40
MgO, %	2.40	2.31	2.24	2.25	2.29	2.25
SO ₃ , %	2.41	2.61	1.00	0.92	1.53	1.57
Na ₂ O, %	4.00	3.82	0.91	0.22	2.85	1.60
K ₂ O, %	0.36	0.32	0.27	0.14	0.36	0.27
Cl ⁻ , %	19.27	18.08	6.63	4.93	10.42	10.15
Free CaO, %	0.15	0.14	8.25	2.86	3.89	0.86

Table 4 - Chemical analysis results of clinkers with different calcination times

Composition	A2.1150.2	A2.1150.4	A3.1150.2	A3.1150.4
LOI, %	1.98	2.40	3.63	2.25
SiO ₂ , %	21.22	20.97	19.87	20.55
Al ₂ O ₃ , %	5.13	5.09	4.99	5.17
Fe ₂ O ₃ , %	3.23	3.09	3.08	3.30
CaO, %	59.77	59.65	54.29	55.14
MgO, %	2.24	2.27	2.20	2.27
SO ₃ , %	1.06	0.99	1.65	1.36
Na ₂ O, %	0.22	0.03	0.88	0.84
K ₂ O, %	<0.01	<0.01	0.13	0.16
Cl ⁻ , %	4.40	5.42	9.14	8.90
Free CaO, %	0.68	0.39	0.67	0.60

Table 5 - Compressive strength of alinite cement mortars

Sample	Compressive Strength, MPa (ksi)		
	2 Days	7 Days	28 Days
A2.1150.2+6%	22.3 (3.23)	30.7 (4.45)	42.3 (6.14)



Fig. 1 - Rod-shaped raw meal in production furnace.

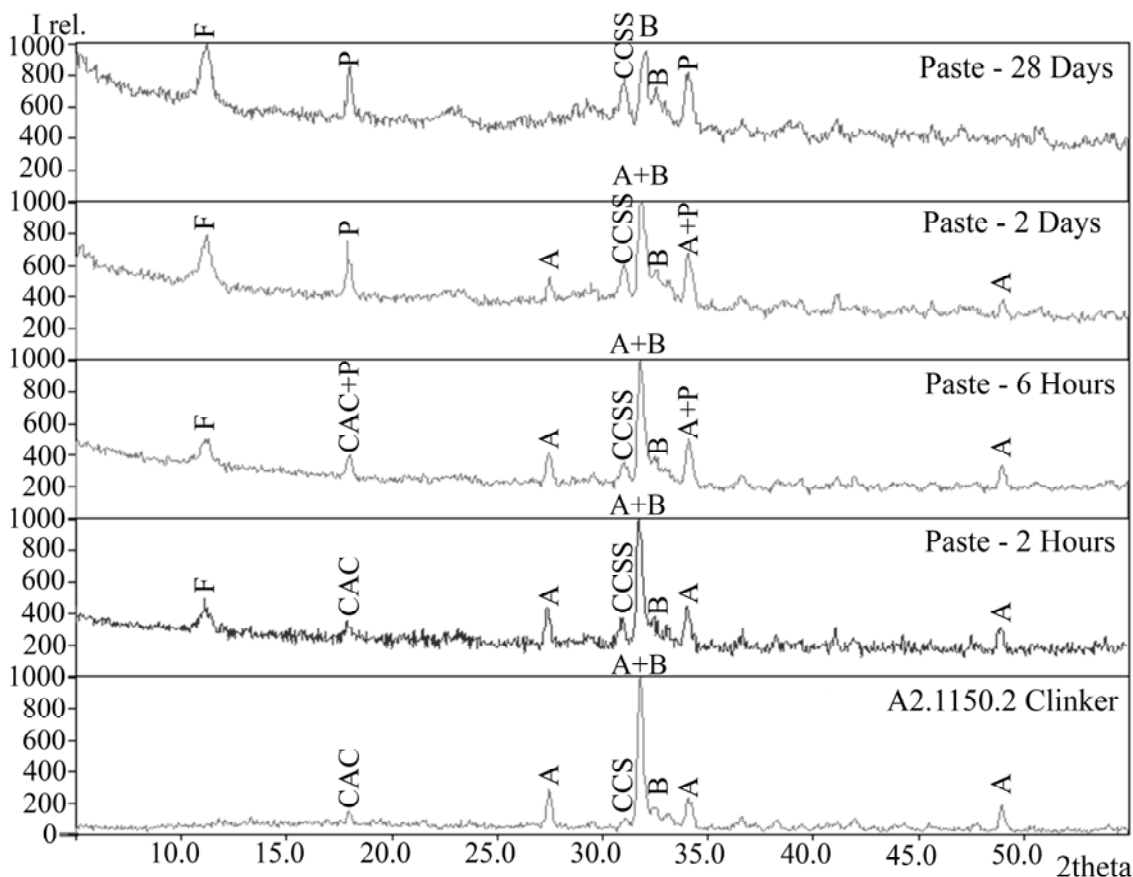


Fig. 2 - XRD patterns of A2.1150.2 clinker and paste of A2.1150.2+6% gypsum after 2 hours, 6 hours, 2 days, and 28 days of hydration. (A = $[Ca_{10}Mg_{0.8}[(SiO_4)_{3.4}(AlO_4)_{0.6}]O_2Cl]$, B = C_2S , CAC = $C_{11}A_7.CaCl_2$, CCS = $Ca_3(SiO_4)Cl_2$, CCSS = $Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$, F = $C_3A.(1-x-y)CaCl_2.xCaCO_3.yCa(OH)_2.10H_2O$, P = $Ca(OH)_2$)

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REUSE OF CERAMIC INDUSTRY SLUDGE AS A COMPONENT IN CEMENT-BASED MATERIALS

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ABSTRACT

Waste management initiatives have arisen around the world in recent years, attendant upon increasingly strict regulations that favour alternative solutions such as diminution and recycling. The sludge generated in ceramic industry glazing and milling, for instance, may be a source of alternative raw materials. The chemical, physical, morphological and mineralogical characterisation of such sludge conducted in this study aimed to determine whether it is appropriate for using in the manufacture of the cement. The kinetics of the pozzolanic reaction in a ceramic sludge/lime system were also assessed. The hydration products ensuing from that reaction induced a steeper rise in flexural strength than compressive strength in the ceramic sludge-bearing material, rendering the end product more flexible and elastic than portland cement.

Keywords: *Cements, pozzolanic activity, supplementary cementitious materials, ceramic waste.*

INTRODUCTION

In addition to the waste or by-products generated during manufacturing, some proportion of products is inevitably regarded as not appropriate for sale and rejected, despite improvements in industrial processes. In recent years initiatives have sprung up around the world to control and regulate waste management, attendant upon increasingly strict legislation that will favour the economics of options such as diminution and recycling. At the same time, in the circular economy ‘waste’ is valorised, acquiring ‘raw material’ status. Moreover, the use of by-products and waste will help meet the objectives of the United Nations Framework Convention on Climate Change (1) designed to minimise greenhouse gas, in particular CO₂, emissions.

The cement industry emits enormous amounts of carbon dioxide, accounting in Spain for 6.4 % of the total anthropogenic emissions of that gas (2). It is also energy- and raw material-intensive. The industry has nonetheless pioneered the use of waste in the several stages of cement manufacture, including applications such as pozzolanic materials as active additions.

Given the proven benefits of their use, pozzolans have been included in cement for thousands of years. The search for alternative pozzolans is a priority today for two reasons: to conserve the environment by reducing raw material quarrying, preventing the depletion of natural resources; and to reuse waste that would otherwise be stockpiled in landfills (3).

European standard EN 197-1 (4) lists the by-products, such as fly ash and silica fume, that can be used as active additions in cement. It also regulates the use of natural burnt

pozzolans, i.e., thermally volcanic materials, clay, schist and sedimentary rocks. As a rule, initially inert clay minerals exhibit considerable pozzolanicity when calcined at temperatures of 600-900 °C and ground to cement fineness. The loss of bound water resulting from calcination induces the breakdown of the crystalline network characteristic of the clay constituents, which are rendered amorphous. Such thermodynamic instability is one of the major explanations for the pozzolanicity of the calcined materials (5, 6).

Heating kaolinite to 450-600 °C gives rise to a product with a disordered structure known as metakaolin (or metakaolinite), one of the most widely researched clays. This phase exhibits pozzolanicity comparable to the activity observed in silica fume (7).

Ceramic industry waste may be regarded as calcined natural materials. Spain's fired clay industry has traditionally produced significant amounts of brick, tiles, blocks and pavers, although output has declined radically since the economic crisis. That notwithstanding, the high percentage of rejects that continues to be generated makes this waste an appealing source of pozzolans for cement and concrete production.

The research conducted on this material has shown that fired clay waste exhibits pozzolanic properties, generating hydration products similar to those observed in the reactions induced by other pozzolans. The effect of the temperature at which the waste is generated has also been studied. Unsuitable kiln temperatures (over- or under-firing) may cause significant variations in the chemical and mineralogical composition of ceramic rejects relative to the product obtained under optimal firing conditions. Nonetheless, temperatures of around 900 °C suffice to activate the clay, conferring pozzolanicity on the waste. Moreover, a number of studies have been conducted on the viability of ceramic waste as a cement replacement, a pozzolan or a filler in concrete roofing tile manufacture (8, 9, 10). Another material studied, sanitary industry waste, also

exhibits 28-day pozzolanicity (11) comparable to silica fume, although at earlier ages the pozzolanic reaction takes place more slowly in the former.

The ceramic industry also generates other types of waste during polishing and glazing that has likewise been studied for use in new cements (12, 13) as an avenue for its valorisation.

Spain has one company that engages in the collection of such sludge and its preparation for use in construction. This study aims to explore the suitability of this by-product as an alternative pozzolanic material. The sludge at issue is the excess generated during milling, and pre-glazing and glazing stages. It consists primarily of the remains of enamel, which have a chemical and mineralogical composition similar to that of the initial enamel, i.e., a vitreous phase plus minerals such as quartz, zircon, feldspars, aluminates, carbonates, and crystalline clayey minerals, along with small percentages of dyes.

RESEARCH SIGNIFICANCE

The authors have conducted a number of studies based on fired clay waste of a variety of origins. Nonetheless, the ceramic sludge generated by the Spanish ceramic industry during glazing and milling has not been previously researched, although the findings to date, discussed hereunder, attest to its good performance as an active addition and open a new line of study in the pursuit of alternative pozzolans to manufacture more sustainable cements.

EXPERIMENTAL

Materials

The following materials were used in this study:

- The ceramic sludge (CS) was a waste material generated during milling, pre-glazing and glazing.

Its fineness was determined on a Sympatec Helos (Bergstadt-Clausthal-Zellerfeld, Germany) 12 KA laser ray particle size analyser, using isopropyl alcohol as the non-reactive liquid.

The X-ray fluorescence-determined chemical composition was found with a Bruker (Karlsruhe, Germany) S8 Tiger spectrometer fitted with a 4 kW rhodium anticathode tube. The chemical composition was found as recommended in the following European standards: chloride and SO₃ content and loss on ignition (LoI): standard EN 196-2 (14); reactive silica and lime, EN 197-1 (4); free lime and soluble phosphates, EN 450-1 (15). The minor elements present in the ceramic sludge, in turn, were analysed on a Varian (Melbourne, Australia) 725-ES inductively coupled plasma optical emission spectrometer (ICP-OES).

Mineralogical composition was analysed on a Bruker (Karlsruhe, Germany) GmbH XS D8 X-ray powder diffractor fitted with a 3 kW (CCu K α 1.2) copper anode and wolfram cathode X-ray generator. Scans were taken at 2 Θ angles of 5° to 60° at a rate of 2°/minute. The standard operating conditions for the voltage generator tube were 40 kV and 30 mA.

Waste morphology was determined on a JEOL (Tokyo, Japan) JSM 5400 scanning electron microscope equipped with an Oxford EDXA energy dispersive X-ray (EDX) analyser.

Pozzolanic activity was determined via an accelerated chemical test consisting on immersing the experimental material in a saturated lime solution at 40 °C for 1, 3, 7, 28, 90, 150 and 360 days, after which the CaO content was determined volumetrically (16). This test can be used to compare the activity of different materials and determine their reaction kinetics.

- A standard EN 197-1 CEM I/42.5 ordinary portland cement (i.e., clinker content

greater than or equal to 95 % and up to 5 % of additions) was used throughout.

- The sand used was as described in standard EN 196-1 (17), i.e., with a silicon content of over 98 % and a particle size of under 0.08 in. (2 mm).

Specimens

The mortar was prepared and batched as per standard EN 196-1 (17), with a cement/sand ratio of 1/3 (wt) and a water/cement ratio of 0.50.

The binder for the reference mortar was 100 % OPC, whilst the experimental mortars contained 80 % OPC and 20 wt% CS. Cement water demand and setting time were tested as described in standard EN 196-3 (18). An IBERTEST (Madrid, Spain) AUTOTEST 200/10 SW test frame was used to determine mechanical strength. Volume stability was established as per standard EN 196-3 (18) instructions.

RESULTS AND DISCUSSION

Further to the laser ray diffraction (LRD) findings depicted in Figure 1, this ceramic sludge had a particle size ranging from 100 μm to 1 μm , with 50 % of the particles under 12 μm and 90 % under 43 μm .

Standard EN 197-1 (4) defines a pozzolanic material as comprising at least 25 wt% reactive silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3), with minor percentages of iron (Fe_2O_3) and other oxides. The ceramic sludge studied, which met all these specifications (Table 1), was highly acidic with a predominance of silicon, aluminium and iron oxides, which together accounted for over 70 wt% of the total.

The waste was also analysed for other chemical compounds that might affect the performance of cement manufactured with ceramic sludge. The findings confirmed that the sludge contained no free lime (<0.3 %) and its sulfate content expressed as SO_3 was 0.10 %, significantly lower than the ceiling specified for type CEM I, II, IV and V

cements. The chloride content was likewise much lower than the ≤ 0.10 % established for all cements, with the sludge contributing just 0.01 %. Loss on ignition, in turn, was not over the 5 % laid down in standard 197-1 (4), although this requisite refers to cements CEM I and II, which would not be the types to be manufactured with CS. The waste consequently met all the standard requirements.

The chemical findings further showed that nearly 10 wt% of the total comprised minor elements, a significant percentage for a potential cement addition. The elements detected included zinc, lead, zirconium and titanium, which are introduced into the sludge at different stages of product manufacture (12) and would have to be monitored by conducting leaching/fixation tests on the cement matrices because these elements can retard the cement hydration. Such tests will be addressed in future research.

The main crystalline compounds detected on the diffractogram in Figure 2 include quartz: with reflections at $2\theta(^{\circ})$ 26.65, 20.85 and 50.14; kaolinite at $2\theta(^{\circ})$ 12.33, 26.21 and 24.74; muscovite at $2\theta(^{\circ})$ 26.83, 8.88 and 34.88; illite at $2\theta(^{\circ})$ 20.03, 35.02 and 24.30; hematite at $2\theta(^{\circ})$ 33.28, 54.23 and 35.74; magnetite at $2\theta(^{\circ})$ 35.45, 62.58 and 57.01; calcite at $2\theta(^{\circ})$ 29.40, 39.40 and 43.4; dolomite at $2\theta(^{\circ})$ 30.99, 30.84 and 24.78; and lastly zirconite at $2\theta(^{\circ})$ 27.0, 20.03 and 35.63.

The SEM study showed that the sludge consisted of spherical particles of different sizes with a predominance of silicon and aluminium, although formations including zirconium and other minor elements were also identified. These results were consistent with the chemical analyses (Figure 3).

The lime fixed by the ceramic sludge studied is given in Table 2. These values are comparable to the 28 day findings observed for additions such as fly ash, with lower early age pozzolanicity (16) than silica fume, which fixes 80 % of the lime in 24 hours (16); sanitary waste, which fixes 70 % (11); ceramic rejects from fired clay roof tile and