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# Effects of modification of alkali activated slag cementing slurries with natural clinoptilolite

## Introduction

Clinoptilolite zeolite is known to have pozzolanic properties. It can react with calcium hydroxide and water forming hydration product with low Ca/Si molar ratio in the range 0.8–1.2 (Ortega et al. 2000). Amorphous C-S-H phase of low Ca/Si molar ratio shows good corrosion resistance (Mróz et al. 2006). Utilisation of zeolites as a cement supplementary material can lead to increase in acid and sulphate resistance of mortars (Mróz et al. 2006).

In drilling industry, cementitious slurries are widely used for boreholes cementing. Slurries used in cementing works have to fulfil a number of requirements connected mainly with rheological parameters in fresh state and high durability in hardened state. The reason for it is that during cementing works the temperature and pressure rise significantly, and also the slurry have to be transported for long distances. High durability is demanded, because hardened structures often works in highly corrosive ambient environment.

In the last few decades, there have been intensive investigations conducted to improve the efficiency of cementing systems. To achieve this goal some new binders were developed (Brylicki et al. 1992). Alkali activated slag cementitious materials are one of them. They are characterized by enhanced durability and very good rheological properties. A new idea is to modify the properties of alkali activated slag matrix with an addition of natural zeolites – clinoptilolite to get more durable geopolymer with enhanced adherence to clayey medium.

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Two kind of zeolitic action are expected. One connected with pozzolanic activity of clinoptilolite – supply of an extra C-S-H phase of low Ca/Si ratio. The second action would be the change of product character, acting as a nucleus of crystallization to change the structure of a product and enhance the adhesion strength to clayey medium. Zeolites formation was found in autoclaved alkali activated cementitious systems (Grutzek et al. 2004; Brough et al. 2001). The environment in cemented borehole is similar to autoclave, so it is possible that the alteration of phase composition will take place.

Other possible way of alkali activated slag binders utilization is immobilization of toxic wastes, e.g. heavy metal ions. Alkali activated slag materials show very good immobilizing properties (Deja 2002). Formation of zeolites may be a way to increase the efficiency of immobilization.

The paper presents the results of investigations on the influence of small zeolites addition on technological properties of slurries in fresh state, and also the influence on strength of hardened pastes. The goal is to evaluate if the zeolites change the properties significantly, and if the influence doesn't disqualify utilization of zeolites as an additive in drilling slurries technology.

## 1. Experimental

### 1.1. Starting materials

In present study the following materials were used:
- ground granulated blast furnace slag of composition showed in Table 1,
- natural clinoptilolite zeolite ($(Ca,K_2,Na_2,Mg)_4Al_8Si_{40}O_{96} \cdot 24H_2O$),
- CEM I 42,5 R according to PN-EN 197-1 standard,
- soda ($Na_2CO_3 \cdot 10\ H_2O$) – technical grade,
- tap water of temperature 20±2°C.

TABLE 1

Composition of GGBFS used in experiments

TABELA 1

Skład chemiczny granulowanego mielonego żużla wielkopiecowego używanego w badaniach

| Compound | Compound content |
|---|---|
| CaO | 44.2% |
| $SiO_2$ | 38.6% |
| $Al_2O_3$ | 8.5% |
| MgO | 6.1% |
| $Fe_2O_3$ | 0.9% |
| $SO_3$ | 2.0% |
| amorphous phase | >90% |
| $CaO+MgO+SiO_2$ | 88.9% |
| $(CaO+MgO)/SiO_2$ | 1.30 |

TABLE 2

Physical and mechanical properties of natural clinoptilolite used in experiments

TABELA 2

Właściwości fizyczne i mechaniczne klinoptilolitu naturalnego użytego w badaniach

| Softening temperature | 1 260°C |
|---|---|
| Melting temperature | 1 340°C |
| Flow temperature | 1 420°C |
| Compression strength | 33 MPa |
| Specific weight | 2 200–2 440 kg/m$^3$ |
| Volume weight | 1 600–1800 kg/m$^3$ |
| Appearance and odour | grey-green, odourless |
| Porosity | 24–32% |
| Relative density | 70% |
| Brightness | 70% |
| Mohs hardness | 1.5–2.5 |
| Water absorbing capacity | 34–36% |
| pH-value | 6.8–7.2 |

TABLE 3

Chemical and phase composition of natural clinoptilolite used in experiments

TABELA 3

Skład chemiczny i fazowy klinoptilolitu nautralnego użytego w badaniach

| Compound | Compound content |
|---|---|
| CaO | 4.0% |
| $SiO_2$ | 68.2% |
| $Al_2O_3$ | 12.0% |
| MgO | 0.9% |
| $Fe_2O_3$ | 1.3% |
| $K_2O$ | 2.8% |
| $Na_2O$ | 0.8% |
| $TiO_2$ | 0.2% |
| Clinoptilolite | 84% |
| Cristobalite | 8% |
| Feldspar | 4% |
| Illite | 4% |
| Quartz | traces |
| Carbonate minerals | < 0.5% |

### 1.2. Samples composition

Samples investigated were of four different water/binder ratios: 0.5; 0.6; 0.8; and 1.0. Clinoptilolite addition was on 4 different levels: 0%, 1%, 3% and 5% by mass in respect to all dry ingredients. Three different activators were used: ordinary portland cement (10% addition by mass in respect to total dry ingredients mass), soda (5% addition by mass in respect to total binder mass) and blended activator – 5% of cement and 5% of soda was also used.

### 1.3. Samples preparation

The measured quantity of water was poured into a plastic bowl. Next, weighted dry ingredients were added in 15–30 seconds. During the dry ingredients addition, the system was stirred with high-speed stirrer at 1200 rpm. After dry ingredients were added, the system was stirred for additional 3 minutes at 7200 rpm.

### 1.4. Methods

For slurries in fresh state following parameters were investigated:
- density – it was measured with Baroid type arm-balance
- relative viscosity – Ford's cup no. 4 – time needed for 150 ml of slurry to flow out of the standardized steel cup; the diameter of outlet is 4 mm
- specific filtration – measured with filter-press Baroid type: the result is the amount of liquid which was squeezed out and the time needed for it
- settlement – the amount of water which lefts over the sedimented slurry in volume % in respect to total slurry volume - measured with a cylinder
- setting time – Vicat apparatus
- rheological properties were measured with rotational viscometer Chan 35 API with 12 shear rates available (between 1.70 $s^{-1}$ and 1022 $s^{-1}$). On the basis of flow curves obtained from measurements, the rheological parameters were calculated using 5 rheological models used to describe the cementing slurries. Each model connects two basic parameters of flow curve – share stress $\tau$ and share rate – $\gamma$.
  - Newton model – $\tau = \eta\gamma$
    - $\tau$ – share stress [Pa]
    - $\gamma$ – share rate [$s^{-1}$]
  - Bingham model – $\tau = \tau_0 + \eta\gamma$
    - $\tau_0$ – yield stress [Pa]
  - Ostwald de Waele model – $\tau = k\gamma^{1/n}$
    - $k$ – consistency coefficient [$Pa \cdot s^n$]
    - $n$ – index [–]
  - Casson model – $\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta\gamma}$
  - Hershel-Bulkley model – $\tau = \tau_0 + k\gamma^{1/n}$

After the flow curve had been measured and each model parameters were calculated, the correlation coefficient was determined for all the models to check how each one of them fits the experimental data. The model with the highest correlation coefficient was considered as the best describing model for a particular mix.

For hardened slurries, mechanical strength was measured:

— compressive strength – with hydraulic press,

— flexural strength – with Michaelis apparatus.

## 2. Tests results and discussion

### 2.1. Properties of fresh slurries

Addition of clinoptilolite practically doesn't change density of slurries, in case of all activators. The density is dependent only on water/binder ratio. Changes in density for slurries modified with zeolites are presented in Fig. 1. The reason that the density doesn't change is that the difference between specific gravities of slag and zeolite is not very high and also the amount of zeolites addition is small. 1–5% is an amount characteristic for admixture rather than additive, so the influence on "bulk" properties like density is not very significant.

Modification of fresh slurry with clinoptilolite leads to increase in stability. In Fig. 2 settlement of slurries is presented. It is visible, that the presence of even small quantities of

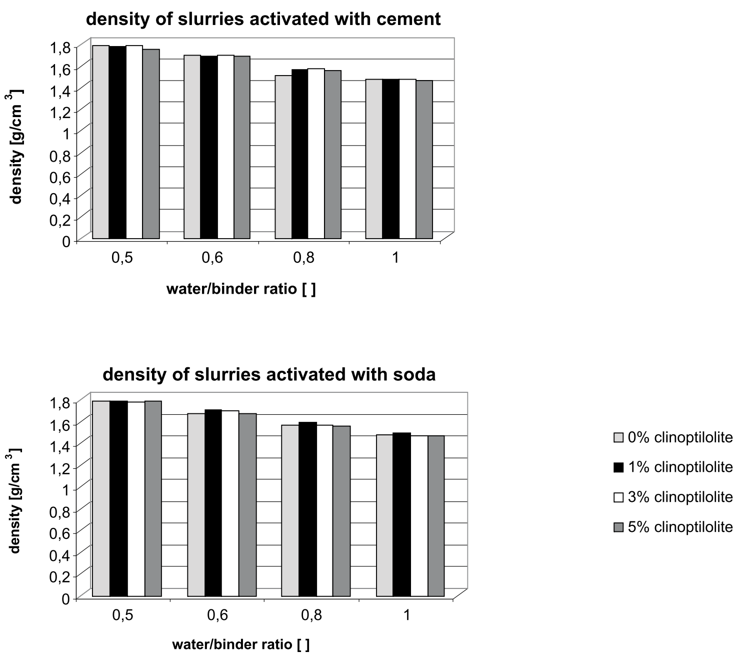


Fig. 1. Density of slurries modified with clinoptilolite

Rys. 1. Gęstość zaczynów modyfikowanych klinoptilolitem

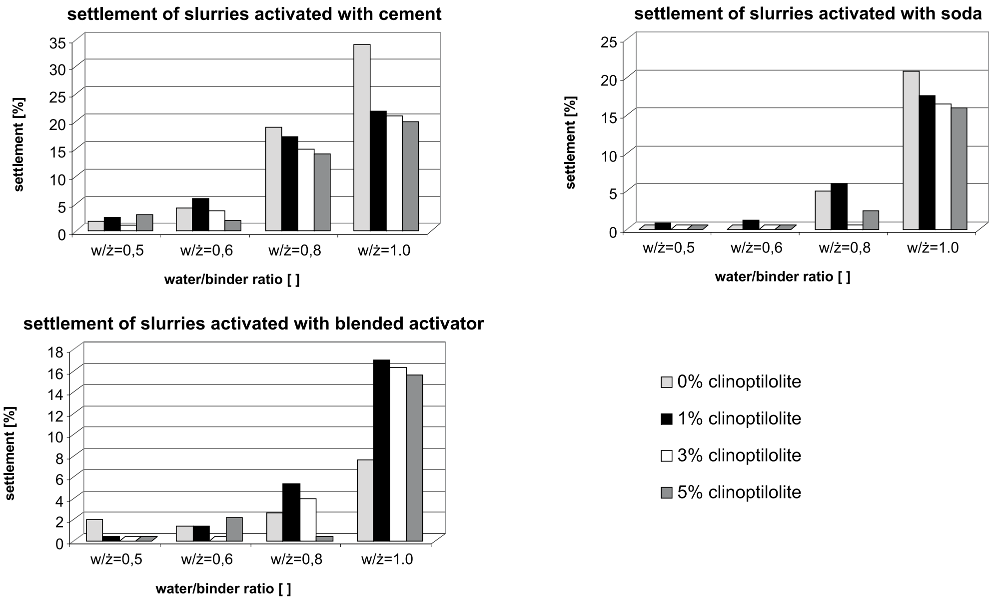


Fig. 2. Settlement of slurries modified with clinoptilolite

Rys. 2. Odstój zaczynów modyfikowanych klinoptilolitem

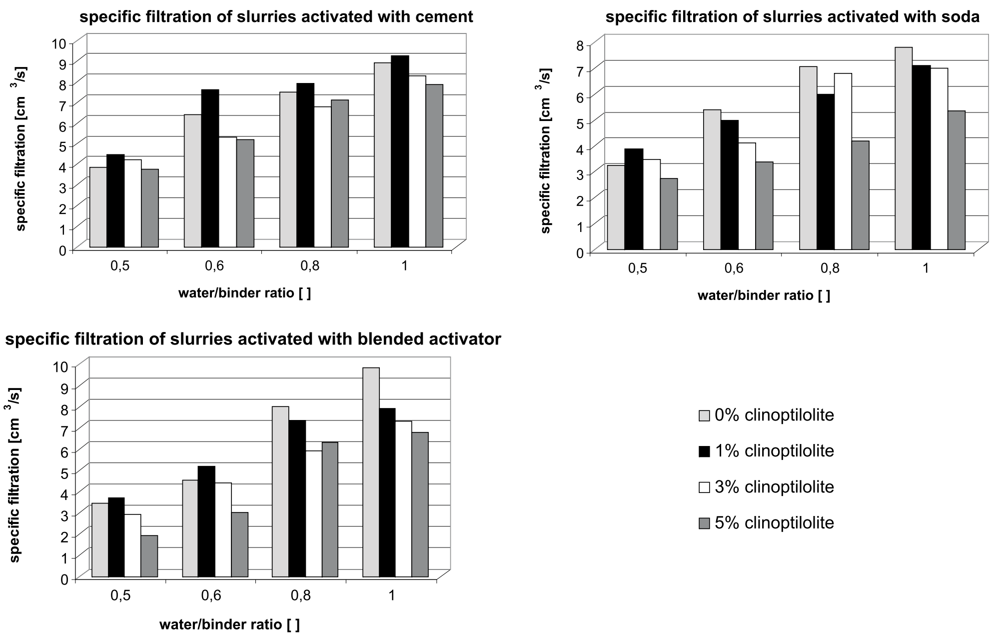


Fig. 3. Filtration of slurries modified with clinoptilolite

Rys. 3. Filtracja zaczynów modyfikowanych klinoptilolitem zeolites tends to decrease the settlement measured with a graduated cylinder. The exception is 1% addition of clinoptilolite, which in case of slurries of lower water/binder ratio causes small increase in settlement. The origin of this phenomenon is yet unknown, but it may be connected with grain size distributions of slurries ingredients. The effect needs to be investigated more carefully.

The influence of clinoptilolite on settlement is more visible for high water/binder ratio. For example in case of slurries of water/binder ratio 1.0 activated with cement the decrease of settlement exceeds 35%. Increased stability when clinoptilolite added is also visible in filtration results. Fig. 3 shows values of specific filtration. Presence of zeolites in general causes the reduction of filtration. The effect is caused mainly by increase of filtration time (specific filtration is a quotient of filtrate volume and filtration time – time needed to squeeze certain amount of filtrate). The volume of filtrate depends mainly on water/binder ratio, and zeolite presence doesn't influence it much. The exception is once again 1% clinoptilolite addition in case of slurries activated with cement. For this amount of zeolites added specific filtration increases. The reason for it is the rise in filtrate volume rather than decrease in filtration time. It suggests that in this system more free water can be present.

Results obtained with Ford's cup use give information about the influence of clinoptilolite on relative viscosity of modified slurries. For lower (0.5 and 0.6) water/binder ratio addition of clinoptilolite causes slight increase in relative viscosity. In case of slurries of higher water/binder ratio there is no influence of clinoptilolite content on relative viscosity. The

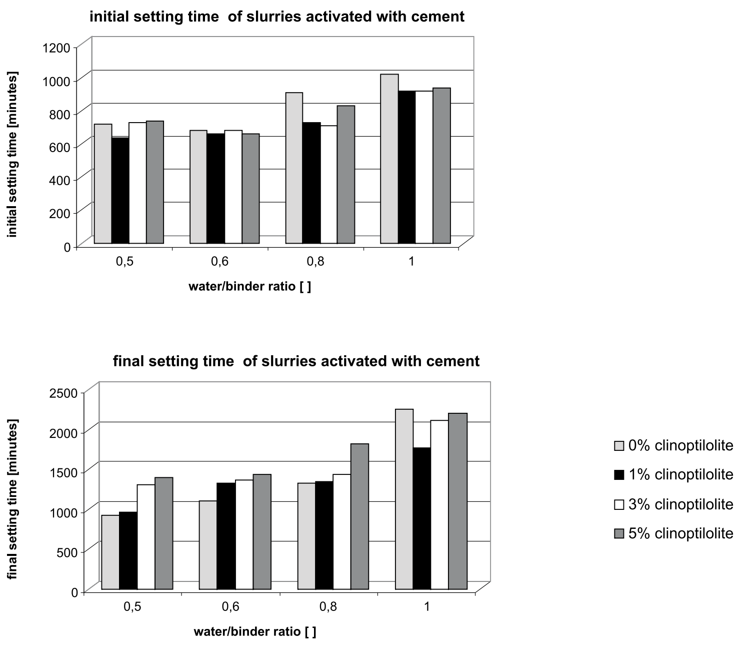


Fig 4. Initial and final setting time for slurries activated with 10% of cement

Rys. 4. Czasy początku i końca wiązania zaczynów aktywowanych 10% cementem

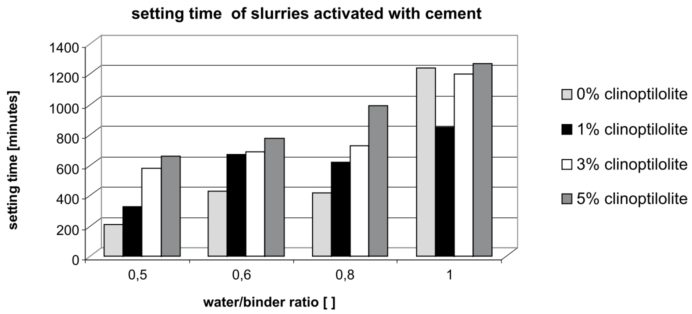


Fig. 5. Setting time of slurries activated with cement

Rys. 5. Czasy wiązania zaczynów aktywowanych cementem

reason for it is probably the fact that in case of low w/b slurries zeolites absorb water (because of their higher water requirement) and decrease the total amount of free water in the paste.

When the amount of water is high (*w/b* = 0.8 and 1.0) this effect is not significant because the amount of water present in the system is far more than the water requirements of all binder composites.

Presence of clinoptilolite zeolites seriously influences the setting behaviour of alkali activated slag slurries. The influence is quite complex. In case of slurries activated with 10% cement addition, presence of clinoptilolite doesn't change (low *w/b* ratios) or leads to shortening of the initial setting time (higher w/b ratios). On the contrary, final setting time is

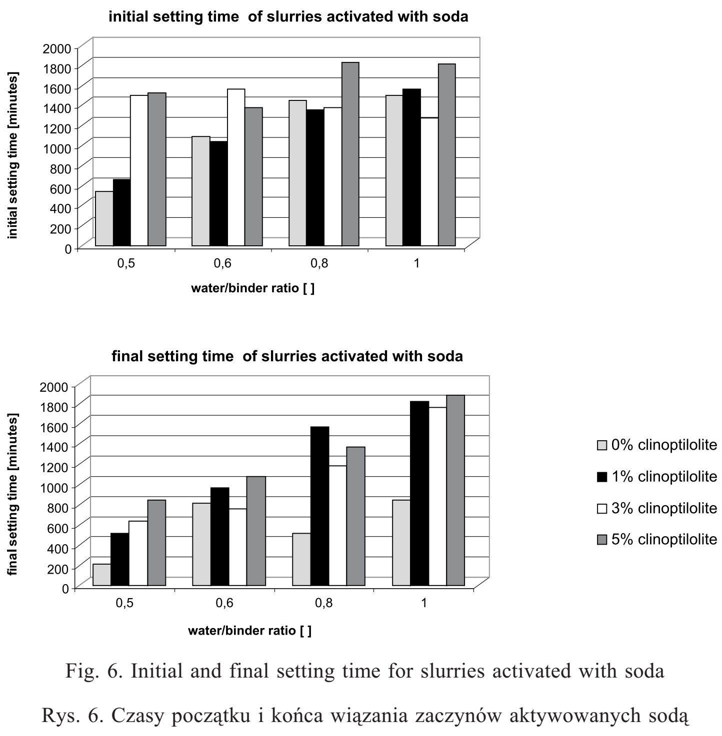


Fig. 6. Initial and final setting time for slurries activated with soda

Rys. 6. Czasy początku i końca wiązania zaczynów aktywowanych sodą

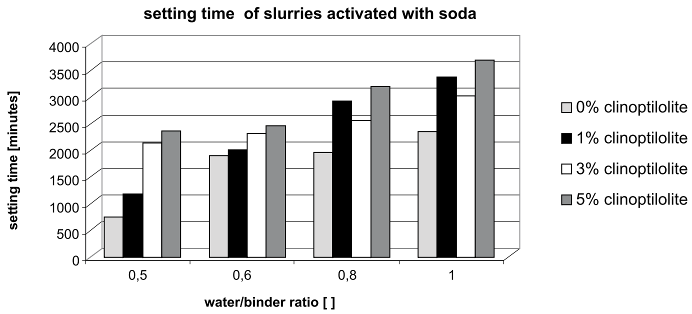


Fig. 7. Setting time for slurries activated with soda

Rys. 7. Czasy wiązania zaczynów aktywowanych sodą

delayed (except w/b ratio 1.0 where it is shortened). In general it leads to increase in setting time length i.e. time between initial and final setting time (see Fig. 5).

In soda activated slurries clinoptilolite markedly delay the final setting time. Initial setting time is also delayed, but to smaller extent (see Fig. 6). The result is that the setting time is increased (Fig. 7).

In general slurries activated with soda set up to two times longer than slurries activated with cement. The influence of zeolites is also stronger in case of soda activated slurries. Slurries activated with blended activator show the shortest setting times. Presence of clinoptilolite alters it very slightly. It tends rather to decrease both initial and final setting times rather than increase them.

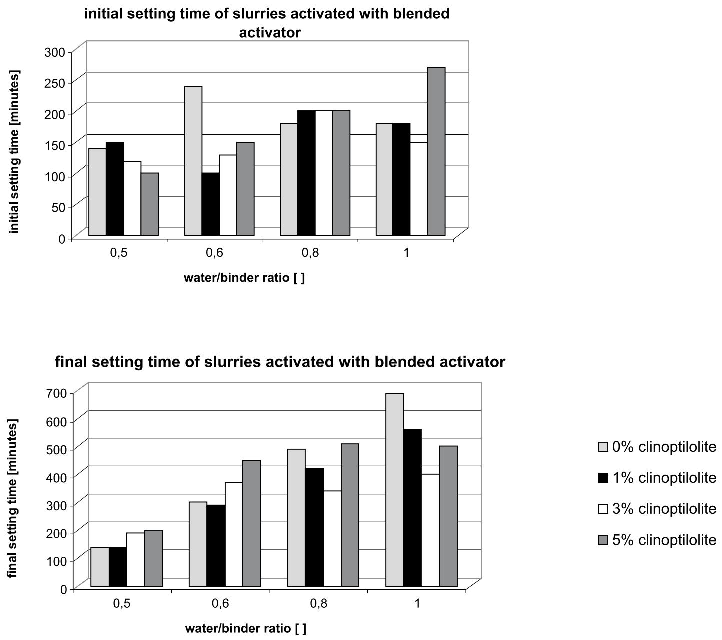


Fig. 8. Inital and final setting times for slurries activated with blended activator

Rys. 8. Czasy początku i końca wiązania dla zaczynów aktywowanych aktywatorem mieszanym

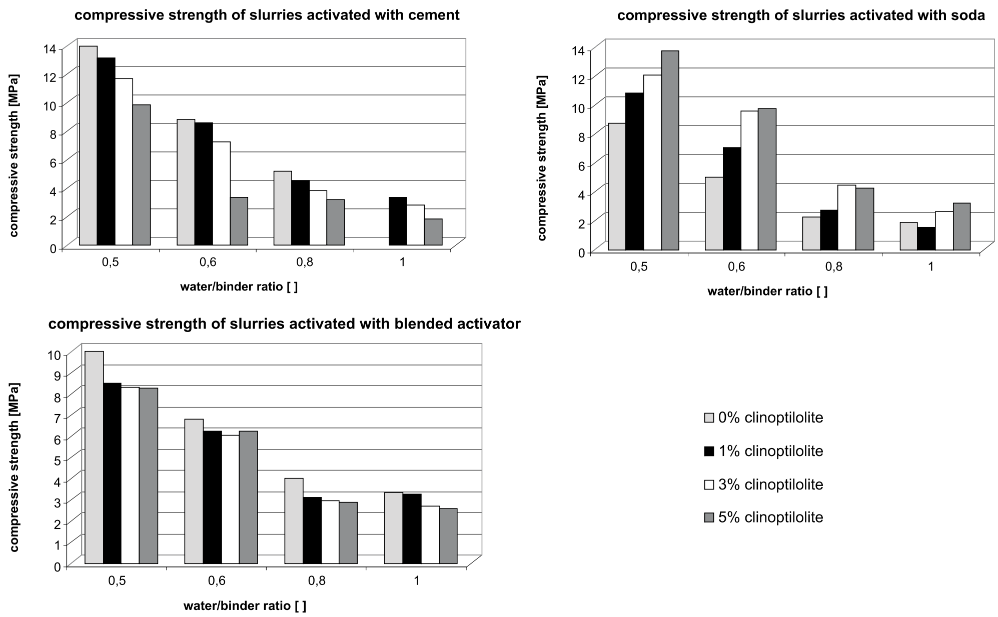


Fig. 9. Compressive strength of hardened slurries after 7 days of curing in water

Rys. 9. Wytrzymałość na ściskanie stwardniałych zaczynów po 7 dniach dojrzewania w wodzie

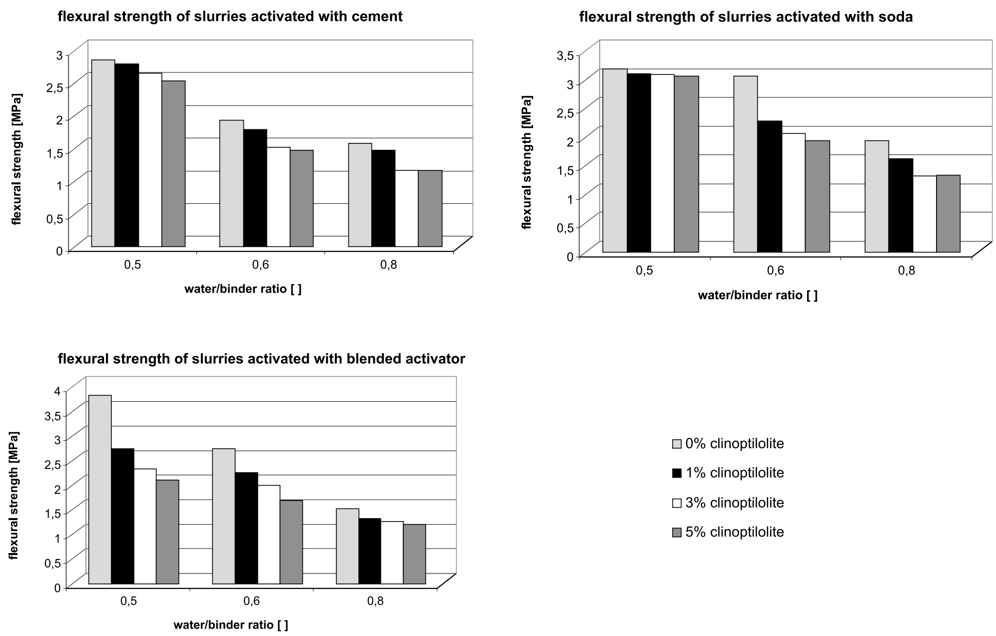


Fig. 10. Flexural strength of hardened slurries after 7 days of curing in water

Rys. 10. Wytrzymałość na zginanie stwardniałych zaczynów po 7 dniach dojrzewania w wodzie

The best rheological model to describe investigated slurries is Casson model. Addition of clinoptilolite doesn't change the rheological parameters significantly. The variations are much smaller than those caused by water/binder ratio. There is also no relationship between rheological parameters and clinoptilolite addition visible.

### 2.2. Properties of hardened slurries

In paper, results of strength determination after 7 days are presented. The presence of clinoptilolite decreases the compressive strength of pastes activated with cement and blended activator. The decrease is proportional to amount of clinoptilolite introduced into the slurry.

Situation is different in case of soda activated slurries. The addition of clinoptilolite causes increase in compressive strength dependent on amount of zeolites. Results presented in Fig. 10 show that zeolites addition decreases flexural strength for all types of activators. The reduction in flexural strength is similarly to compressive strength, proportional to amount of zeolites introduced.

### 2.3. Microstructure investigations

Microstructure investigations were performed using JEOL 5400 electron microscope. Samples were dried, then crushed. Freshly obtained fracture after coating with carbon was

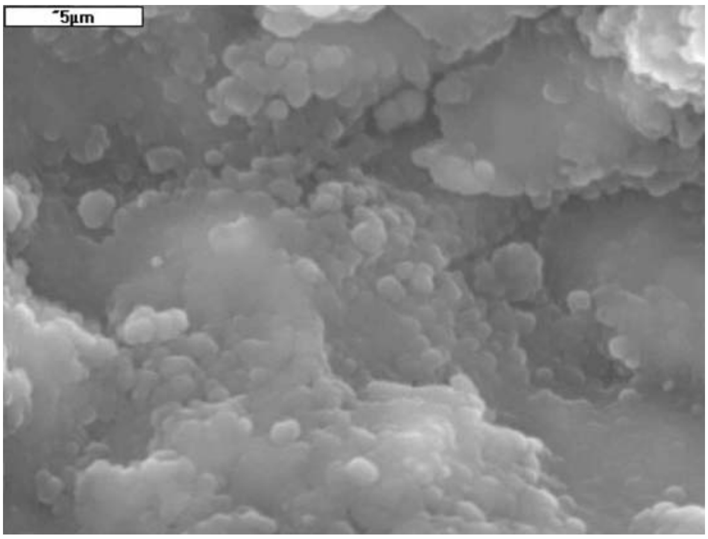


Fig. 11. C-S-H phase in paste activated with soda modified with 1% clinoptilolite addition; cured 120 days in water

Rys. 11. Faza C-S-H w zaczynie zawierającym 1% klinoptilolitu, aktywowanym sodą; zaczyn dojrzewał 120 dni w wodzie

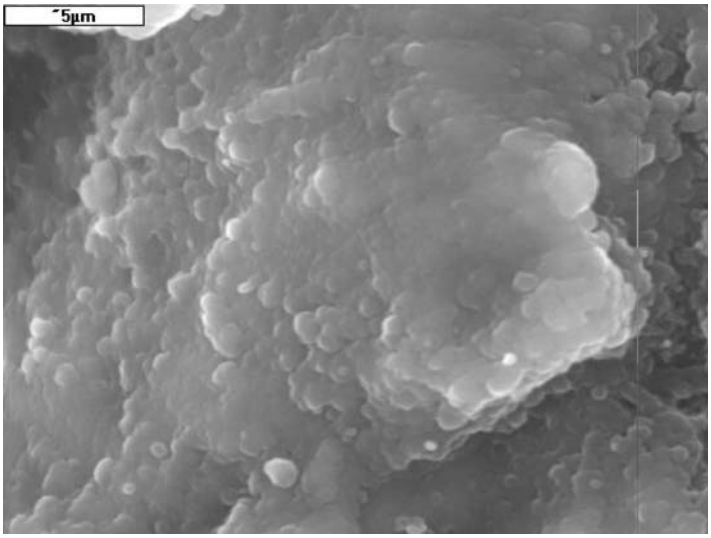


Fig. 12. C-S-H phase in paste activated with cement, modified with 1% clinoptilolite addition; cured 120 days in water

Rys. 12. Faza C-S-H w zaczynie zawierającym 1% klinoptilolitu, aktywowanym cementem; zaczyn dojrzewał 120 dni w wodzie

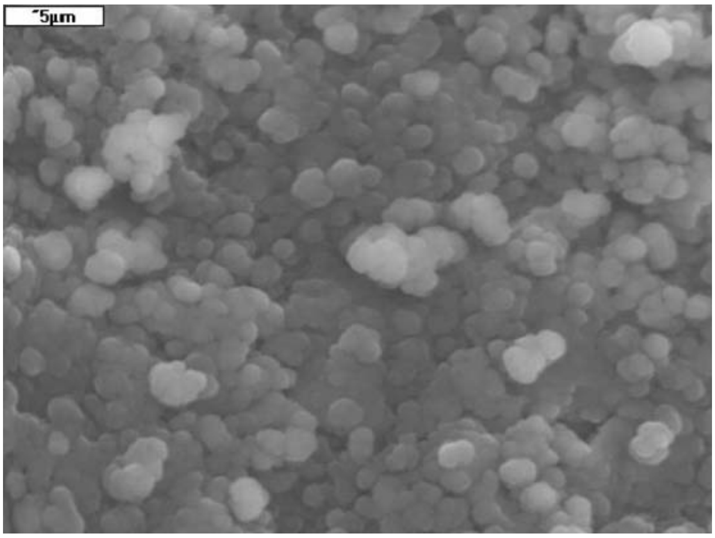


Fig. 13. C-S-H phase in paste activated with blended activator modified with 5% clinoptilolite addition; cured in water for 120 days

Rys. 13. Faza C-S-H w zaczynie z 5% dodatkiem klinoptilolitu, aktywowanym aktywatorem mieszanym; zaczyn dojrzewał 120 dni w wodzie

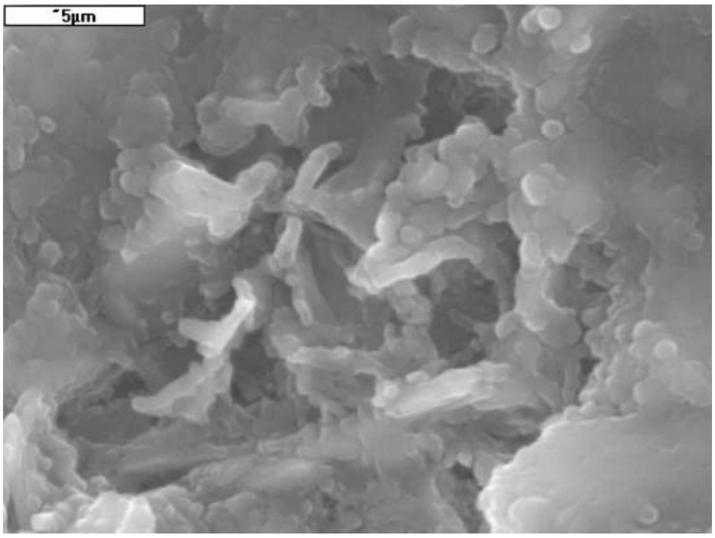


Fig. 14. Elongated features within cement activated, 5% clinoptilolite paste;
elongated features rich in Ca and Al; surrounding C-S-H phase of C/S molar ratio = 1.4

Rys. 14. Podłużne produkty hydratacji w zaczynie zawierającym 5% klinoptilolitu, aktywowanym cementem;
podłużne produkty bogate w Ca i Al; otaczająca faza C-S-H o molowym stosunku C/S = 1,4

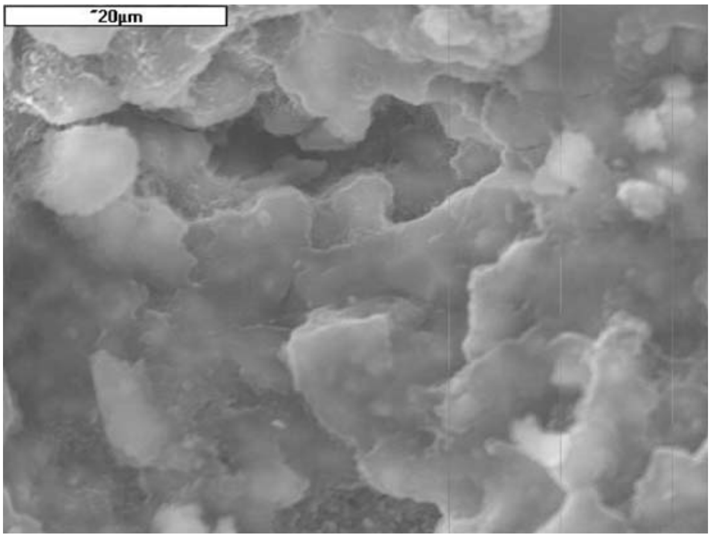


Fig. 15. Soda activated slag paste modified with 1% addition of clinoptilolite – C-S-H of C/S ratio 0.9;
cured in water for 120 days

Rys. 15. Zaczyn z dodatkiem 1% klinoptilolitu, aktywowanym sodą, faza C-S-H o stosunku C/S = 0,9;
zaczyn dojrzewał 120 dni w wodzie

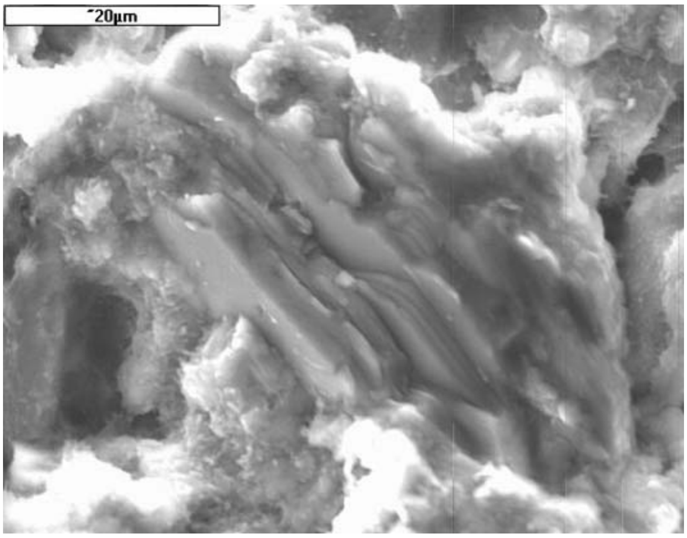


Fig. 16. Portlandite and fibrous C-S-H visible in cement activated 1% clinoptilolite slag paste; cured in water for 28 days

Rys. 16. Portlanlyt i włóknista faza C-S-H uwidocznione w zaczynie zawierającym 1% klinoptilolitu, zaczyn aktywowanym cementem; zaczyn dojrzewał 28 dni w wodzie

observed in secondary electron mode. Sample images are shown in Figures 11–16. CSH of type IV according to Diamond was found as a main constituent of hardened cement pastes. In cement activated samples some phases originate form cement hydration were also found. Portlandite and fibrous C-S-H phase are visible in Fig. 16. Microstructure of zeolites modified pastes is dense and compact (see Fig. 11 and Fig. 12). Soda activated pastes seem to be less porous and cracked in comparison to cement activated samples.

## Conclusions

Modification of alkali activated ground granulated blast furnace slag pastes with natural zeolite – clinoptilolite leads to modification of some properties of resulting material. Stability of slurries is increased, what is manifested by decrease in specific filtration and settlement. The hydration kinetics are also altered, and setting times are delayed, even up to two times. Density doesn't change with addition of clinoptilolite in the range used in the experiments. Presence of natural clinoptilolite doesn't change the rheological properties significantly. For all slurries Casson model was found to be the best to describe the flow properties. No straight relationship between rheological properties of slurries and zeolites content was found.

Clinoptilolite modification leads to decrease in both compressive and flexural strength measured after 7 days. The decrease is proportional to the amount of clinoptilolite introduced to the slurry. The only exception is slurries activated with soda where compressive strength is rising with the increasing zeolite fraction. Microstructure of hardened pastes is compact and densely packed, consisting mainly of C-S-H type IV according to Diamond. Some features originate form hydration of cement used as an activator can be found in cement activated pastes.

In general clinoptilolite can be used as an additive in cementing slurries technology. In further parts of investigations influence of zeolites on permeability and chemical resistance will be conducted. Hydration experiments in elevated temperature and water vapour pressure are planned in order to simulate borehole environment and investigate the influence of clinoptilolite on hydration of slurries when used in real cementing works.

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### EFFECTS OF MODIFICATION OF ALKALI ACTIVATED SLAG CEMENTING SLURRIES WITH NATURAL CLINOPTILOLITE

Key words

Clinoptilolite, alkali–activated slag, drilling operations, durability, zeolites

Abstract

Alkali activated slag slurries for boreholes cementing were modified with natural zeolite – clinoptilolite. Three different activators: ordinary portland cement, soda and blended activator (cement + soda) were used. In present paper results of investigations on the influence of clinoptilolite modification of alkali activated slag slurries are described. Natural clinoptilolite was introduced to alkali activated slag pastes in quantities between

1 and 5% in respect to dry ingredients mass. Properties of pastes both in fresh and hardened state were examined. Microstructure studies were also conducted.

Addition of natural clinoptilolite slightly changed the workability of slurries. It seriously influenced setting behaviour of the slurries. Details are presented in the article. Casson model was found as the best model to describe the rheological properties of fresh slurries. Clinoptilolite causes reduction in 7 days strength (except compressive strength of soda activated slurries).

**EFEKTY MODYFIKACJI ALKALICZNIE AKTYWOWANYCH ZACZYNÓW WIERTNICZYCH NATURALNYM KLINOPTILOLITEM**

Słowa kluczowe

Klinoptilolit, alkalicznie aktywowane żużle wielkopiecowe, wiertnictwo, trwałość, zeolity

Streszczenie

Alkalicznie aktywowane zaczyny do cementowania otworów wiertniczych modyfikowano dodatkiem naturalnego zeolitu klinoptilolitu. Używano 3 różnych aktywatorów: cement portlandzki CEM I, sodę techniczną oraz aktywator mieszany – CEM I + soda. Artykuł prezentuje wyniki badań wpływu dodatku klinoptilolitu na właściwości alkalicznie aktywowanych zaczynów żużlowych. Naturalny klinoptilolit był wprowadzany w ilościach pomiędzy 1 a 5% w stosunku do suchej masy spoiwa. Badano właściwości zaczynów zarówno w stanie świeżym jak i stwardniałym.

Dodatek naturalnego klinoptilolitu nieznacznie zmienia urabialność zaczynów. W znacznym stopniu wpływa zaś na czasy wiązania. Szczegóły przedstawiono w artykule. Dodatkowo klinoptilolit powoduje spadek wytrzymałości po 7 dniach w zaczynach aktywowanych cementem, zaś podniesienie wytrzymałości 7-dniowej zaczynów aktywowanych sodą. Za najlepszy model reologiczny opisujący zachowanie badanych zaczynów uznano model Cassona.