The Influence of Zeolitic Spent Refinery Admixture on the Rheological and Technological Properties of Steel Fiber Reinforced Self-Compacting Concrete

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Abstract—By planning this experimental work to investigate the effect of zeolitic waste on rheological and technological properties of self-compacting fiber reinforced concrete, we had an intention to draw attention to the environmental factor. Large amount of zeolitic waste, as secondary raw materials are not in use properly and large amount of it is collected without a clear view of its usage in future. The principal aim of this work is to assure, that zeolitic waste admixture takes positive effect to the self-compacting fiber reinforced concrete mixes stability, flowability and other properties by using the experimental research methods. In addition to that a research on cement and zeolitic waste mortars were implemented to clarify the effect of zeolitic waste on properties of cement paste and stone. Primary studies indicates that zeolitic waste characterizes clear pozzolanic behavior, do not deteriorate and in some cases ensure positive rheological and mechanical characteristics of self-compacting concrete mixes.

Keywords—Self compacting concrete, steel fiber reinforced concrete, zeolitic waste, rheological properties of concrete, slump flow.

I. INTRODUCTION

SELF-COMPACTING CONCRETE (SCC) has successfully entered into industry, and in some countries it already predominates against conventional concrete mixture, since its development. Yet, use of another type of concrete is becoming more widespread, i.e. use of concrete reinforced by dispersive fiber. Combining the advantages of the two types of concrete, a fiber reinforced self-compacting concrete (FRS SCC) is therefore obtained. Its properties have been widely investigated lately [17], [20], [15], [7], [2]. The most promising and attracting most of researchers’ interest issue in this field is the ability to employ the flow of self-compacting concrete in order to form a steadily aligned structure of dispersive fiber in a concrete. The main objective is to make the dispersive fiber align in a direction parallel to the flow of mixture by using the kinetic energy of flowing concrete mixture. One of the key factors influencing the results in solving this issue is the rheological properties of the concrete mixture. Scientific literature suggests that when increasing the amount of steel fiber in the SCC mixture, the slump flow of the mixture decreases and the viscosity of the mixture increases [1], [19]. It has been also recognized that higher length and diameter (L/D) ratio of the fiber worsens the workability of the mixture [1], [2], [21]. Usually, SCC mix composition can be characterized by these facts: higher amount of small particles increased W/B (water/binder) ratio and relatively higher amount of chemical admixtures. Blast furnace slag, fly ash or silicea fume are often used as micro fillers. Natural or synthetic zeolite is also found when used as a micro filler.

Zeolites are classified as aluminum silicates. Large specific Blaine surface and high porosity is characteristic to zeolites. Silicic and aluminum oxides form the larger part of them. Similarly to silica fume or blast furnace slag, these materials possess pozzolanic reaction properties. Most of the scientific research has been carried out with clinoptilolites that are mined in different spots of the world as a rock of fossil origin [5]. Considerably less research has been carried out with zeolite, mostly synthetic, that is used in the process of oil cracking. In one of the researches [13], zeolites, considered as production waste (hereinafter – zeolitic waste), used at oil treatment plant in Spain have been investigated. The following is the chemical composition of this material: SiO₂ – 48.2%, Al₂O₃ – 46.0%, Fe₂O₃ – 0.95% and other. High porosity and water absorption of zeolitic material has been also observed and that makes an impact to workability of fresh state concrete mix. The specific gravity of the material is 2450kg/m³, meanwhile the bulk density is only 863kg/m³. Authors distinguish the following advantages of zeolitic waste, obtained from production: environmental dimension (lower cement consumption, reduced energy consumption, reduction of carbon dioxide emissions), economical dimension (the price of zeolitic waste is relatively lower than of cement), technological advantages (improved properties of concrete mixture and hardened concrete, as well as of grout).

The material is usually used as a catalyst, and it is the waste obtained from the process of catalytic cracking in oil treatment industry. Application of zeolites is largely increasing. Due to its specific properties, today it is one of the most promising components at creating the latest advanced construction technologies (high-performance concrete, self-compacting concrete, specific concretes that “absorb” heavy metals or suppress radiation exposure, and others). These technologies of application of zeolite are under development, and natural as well as synthetic zeolites will be used in these technologies.
During the technological oil refinery process at oil treatment plants, zeolites tend to be tainted with various impurities including heavy metals, therefore, in order to use them in construction materials, different issues may arise related to harmfulness, technological factors, etc. In terms of harmfulness, it is the most advisable to use it in construction materials intended for industrial purposes [3].

From environmental perspective, zeolitic catalyst waste disposal is an extremely important issue. Every year, there are about 400,000 tons of various catalyst waste forming at oil treatment plants [11]. With quickly increasing oil industry, the amounts of spent catalyst rise inevitably. At JSC “Mažeikių Nafta” in Lithuania, there are about 200 tones forming in a year. Catalyst waste from JSC “Mažeikių Nafta” is different in its shape (spheres, bars, and tubes), measurements (e.g., spheres from 10µm to 40mm) and chemical composition [3].

One of the ways to utilize this zeolitic waste is to use it at concrete production. Researches show that in most cases, natural zeolites influence the rheological properties of SCC mix. During an experiment, authors [18] noticed that when replacing part of the cement (5, 10, 15, 20%) by natural zeolite, the slump flow of the mixture decreases. Authors mostly compensate this decrease by increasing the amount of superplasticizer [16], [18], [5], [13], [14]. It has been noticed that when maintaining equal slump flow of the mixture by means of superplasticizer, the flow time t_{500} of the mixture significantly increases. Comparing the mixture without added natural zeolite and including 20% of this material, the flow time t_{500} has been greater by 43% on average. During the V-funnel test, flow time t_{500} of mixture has increased by 41% on average. The influence of natural zeolite on the slump flow of mixture can be reduced by means of using higher amount of superplasticizer [16], and reduced slump flow of mixture when part of cement is replaced by increasingly higher amount of zeolite can be explained by the fact that physical ability of retaining water of this additive is higher [5], [16]. It has been recognized that in case the granulometric contents of cement and zeolite is similar, the specific surface area indicated by Blaine method is several times larger. This can be attributed to porous crystal structure of zeolite which absorbs more of the free water in the mixture. The other reason might be the fact that the density of zeolite is lower than that of cement. When, part of cement is replaced by material of lower density, the volume of the mixture increases, while the amount of water remains the same [16].

Natural or synthetic zeolites, as well as silica fume, silica fly ash or blast furnace slag, involve pozzolanic properties. The new C-S-H compounds obtained during the reaction with cement hydration product Ca(OH)₂ influence the strength properties positively. It is argued that the increased compressive strength of concrete mixtures including natural zeolite additives can be better used when the water and binding agent ratio is lower [18]. In this research, the results of strength properties of the samples after 28 and 90 days of curing indicate that the most effective amount of natural zeolite replacing cement is 10%. Reduced amount of cement determine lower compressive strength in the initial phase of concrete curing (to 7th-28th day), yet in later phases, the increase of compressive strength has been observed in the samples where zeolite additive had been used [5], [6]. Results show that after 7 days of curing, the highest compressive strength has been registered in the sample containing 10% of zeolite replacing cement, after 28 and 56 days – including 15%, after 90 days – 20% of zeolite [5]. Other authors [9], [14], [10] present similar tendencies. While increasing the amount of natural zeolite in the mixture, the water absorption of hardened grout and concrete decreases significantly [18], [10], [5]. It is also interesting to see that although after 28 days of curing the decrease in density has been observed, the water absorption in the samples containing natural zeolite additive has also decreased. Again, this is explained by the reaction between SiO₂ or Al₂O₃ and calcium hydroxide, as well as increased amount of C-S-H gel which forms relatively dense structure of the binding material [5]. Moreover, use of natural zeolite can considerably expand the binding time of binding of cement paste [5], [16].

II. MATERIALS

The following fine aggregates have been used in concrete mixtures: fraction 0/2 and 0/4, and coarse aggregate – gravel of fraction 4/16. In order to obtain a continuous curve of granulometric composition of fine and coarse aggregates containing higher amount of fine particles, the following comparative amounts of fillers have been calculated using analytical and numerical methods according to their mass: sand 0/2 – 7.1%, sand 0/4 – 47.3% and gravel 4/16 – 45.6%. Overall curve of granulometric composition of fillers is presented in Fig. 1.

The main binding material for investigation was used – cement CEMII/A-LL 42.5R. In this research, synthetic zeolitic waste has been used which performs a catalyst role in oil refinery process. The material has been acquired from oil treatment plant JSC “Mažeikių Nafta” based in Lithuania. Granulometric composition curves of cement and zeolitic waste are presented in Figs. 2, 3, and elemental composition of zeolitic waste – in Table I. The zeolitic waste grain sample has been photographed by means of scanning electron microscope (SEM). The picture shows spherical particles dominating in zeolitic waste powder (see Fig. 4).

Steel fiber and standard hooked end geometrical shapes have been used. Fiber length L=50 mm, diameter d=1mm.

![Fig. 1 Overall granulometric composition distribution of fine and coarse aggregates](image-url)
III. EXPERIMENTAL PROGRAM

The experimental program involves two major parts: cement paste and hardened cement paste as well as concrete mixture investigation. The main aim was to identify technological properties of SCC mixture, when part of the cement in the mixture is replaced by zeolitic waste, adding steel fiber. As zeolitic waste is characterized by large specific surface area and ability of absorbing and retaining water, paste of standard consistence has been tested. The research has been carried out in order to develop the concrete mixture composition more precisely when changing only the amount of zeolitic waste additive, leaving the W/B (water/binder) ratio and amount of superplasticizer intact. It also allowed forecast the change of the technological properties of mixture more precisely. Mechanical properties of hardened cement paste have been identified in the research, when W/B=SCCP (standard consistence of cement paste) and W/B=const.

When experimenting with concrete mixtures, the main – comparative composition (see Table II) has been chosen, in which with zeolitic waste additive amounting from 0 to 30%, SCC mixture has not shown segregation, the mixture was workable and other positive properties have been ensured. Properties of these mixtures have also been tested after adding steel fiber.

IV. RESULTS AND DISCUSSION

A. Standard Consistence of Cement Paste Tests

Natural and synthetic zeolites are characterized by porous structure which is capable of retaining high amount of water. During the experiment, part of cement (0, 10, 20, 25 and 30%) has been replaced by zeolitic waste. Vicat apparatus, complying with EN 196-3:2005 standard, has been used in the experiment. Every mixture has been stirred for total 180 sec. by making stops according to EN standard. When Vicat apparatus rods would sink 6±2mm above the plate bottom, such consistence paste was considered as standard. The presented diagram (Fig. 5) shows increasing water demand tendencies when part of cement has been replaced by zeolitic waste, and these tendencies are similar to those tendencies described by other scientists [13], [16], [12], [8], [4]. Due to its porous structure and large specific surface area, with increasing the amount of zeolitic waste, the water demand for obtaining a standard composition paste constantly increases.
B. Mechanical Properties Investigation of Hardened Cement Paste

Compression strength of binding agent (cement + zeolitic waste) samples, after 7, 28 and 90 days of curing under standard conditions, has been identified in two cases: a) when the W/B ratio of the mixture = SCCP, and b) when W/B = const. = 0.354. While analyzing the compressive strength when W/B = SCCP, substantial increase of strength can be observed when the amount of zeolitic waste replacing cement is 10%. Change in compressive strength after 28 days of curing under standard conditions, compared to sample without zeolitic waste, increased by 17.1%, and after 90 days it increased by 12.4% (see Fig. 6).

With increased W/B ratio from 0.282 to 0.354, and the amount of zeolitic waste – from 0 to 30% (replacing cement), the decrease of compressive strength after 28 days is only 2.7%, and only 6.2% after 90 days of curing. These obtained results do not tend to contradict other scientific works. Most of them, when using natural and synthetic zeolites, also indicate the increase of compressive strength when replacing cement by zeolitic waste by 5-20% [5], [6], [9].

Increase of compressive strength when replacing part of cement by reactive zeolitic waste additive can be explained by pozzolanic reaction and denser granulometric composition of the mixture, and also by the change in density. Although the density of synthetic zeolitic waste used in the research is by ~34% lower than that of cement, when replacing 10% of cement by this additive, the highest compressive strength of hardened sample has been obtained (see Fig. 7). In this case, increase in density after 90 days, compared to control sample, is 5.5%.

Fig. 8 shows the change of compressive strength of the samples where W/B = const. = 0.354. As it can be seen, before the 90th day of curing, samples without zeolitic waste additive show higher compressive strength, yet, after the 90th day, the sample containing the amount of 30% of zeolitic waste is virtually equal to control sample in terms of compressive strength.
TABLE II

SCC Mixture Compositions (to Produce 1m³ of Mixture) for Identifying Technological Properties of the Concrete

<table>
<thead>
<tr>
<th>Concrete mix stabilizer (SB)***, %</th>
<th>Concrete mix</th>
<th>Cement, kg</th>
<th>Water, kg</th>
<th>Sand 0/2, kg</th>
<th>Sand 0/4, kg</th>
<th>Coarse aggregate 4/16, kg</th>
<th>Steel fiber, kg</th>
<th>Zeolitic waste, % *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mix A with different amounts of steel fiber **</td>
<td>410</td>
<td>150</td>
<td>133.14</td>
<td>893.94</td>
<td>859.90</td>
<td>0</td>
<td>15</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25</td>
<td>0</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Mix B with different amounts of zeolite. Steel fiber 0 kg/m³ **</td>
<td>369</td>
<td>150</td>
<td>133.14</td>
<td>893.94</td>
<td>859.90</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Mix C with different amounts of zeolite. Steel fiber 25 kg/m³ **</td>
<td>369</td>
<td>150</td>
<td>133.14</td>
<td>893.94</td>
<td>859.90</td>
<td>25</td>
<td>20</td>
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<td></td>
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<td>20</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>

* the indicated percentage of cement replaced by zeolitic waste, i.e. 10, 20, 30%.
** properties of each mixture have been investigated twice: once with 2.0% of added superplasticizer (“Sika” ViscoCrete-D187), and the second time – with 2.5%.
*** “Sika” Stabilizer 4R.

A. Properties of SCCMixes

Investigating technological properties of the mixtures has been started with experimental mixture without zeolitic waste (mixture A). With these mixtures, attempts to identify the influence of steel fiber on slump flow of the mixture have been made employing the Abhram’s cone method and the J-ring method (see Table II). As we have already discussed the results of some scientists’ works in the introductory part of this work, the obtained results could be expected. When using 2.0% of superplasticizer, the initial slump flow of the mixture without steel fiber was 66.0cm, and after increasing the amount of steel fiber to 35kg/m³, slump flow of the mixture was 49.0cm. Decision has been made to increase the amount of superplasticizer to 2.5%, and to repeat the experiment. Stability of each mixture has been tested by three-cylinder method in order to investigate the stability and segregation of concrete mixture. Slump flow of the mixture dependency on the amount of steel fiber is presented in Fig. 9.

Along with slump flow of the mixture test, other experiments have been also carried out:
- J-ring slump flow.
- J-ring blocking ratio Bj.
- Flow time t₅₀₀.
- Density of fresh concrete mix (see Fig. 11)
- Determination of fresh state concrete segregation by using three-cylinder method.

Figs. 9, 10 show that steel fiber both decreases the slump flow of the mixture, and increases the flow time t₅₀₀.

Fig. 9 Slump flow of the mixture dependency on the amount of added steel fiber without zeolitic waste

Fig. 10 Flow time t₅₀₀ of the mixture dependency on the amount of added steel fiber

Other investigation was intended for identifying the zeolitic waste influence on rheological properties of the mixture (mix B). After carrying out the experiments, it cannot be generally...
ascertained in what way zeolitic waste changes the viscosity properties of a mixture. When using 2.0% of superplasticizer, slight decrease of slump flow of the mixture has been observed, while in those mixtures including 2.5% of added plasticizer and increasingly higher amount of cement replacing by zeolitic waste, significant slump flow of the mixture has been observed (see Fig. 12). Yet, in both cases, when increasing the amount of zeolitic waste, the mixture tended to become “slower” and more viscous. The mixture including zeolitic waste would stop flowing on the measuring table in significantly greater time. This fact is also supported by significantly increasing flow time of the mixture (see Fig. 14).

The third phase of the investigation (mix C) was intended to investigate the complex effect of zeolitic waste and steel fiber on technological properties of SCC mixture. In this case, amount of 25kg/m³ has been chosen, and the produced mixtures contained 10, 20 and 30% of cement replacing zeolitic waste. Complex effect of zeolitic waste and steel fiber on slump flow of the mixture has been negative (see Fig. 13), although, this decrease of slump flow of the mixture has been determined by increased amount of steel fiber as opposed to increase of the amount of zeolitic waste in the mixture. Tendency of increasing slump flow of the mixture from 70 to 79cm has been observed in mixtures without steel fiber with concentration of superplasticizer being 2.5% and when increasing the amount of zeolitic waste (from 0 to 30%). Meanwhile, decrease of slump flow of the mixture from 63 to 60cm in the mixtures containing 25kg/m³ of steel fiber has been observed.
Due to its porous structure and large specific surface area, zeolitic waste produced in the process of oil cracking is greatly capable of retaining water. When replacing cement by 30% of zeolitic waste, water demand in standard consistency paste has increased by 20.3%.

Examination of compressive strength of hardened cement paste where W/B ratio was equal to SCCP (standard consistency of cement paste) after 28 days of curing showed that when replacing 10% of cement by zeolitic waste, increase of strength is 17.1% on average. Moreover, when replacing 10% of cement by this additive, the obtained density of the hardened sample has been the highest, despite the fact that the density of zeolitic waste used in the research has been ~34% lower than that of cement.

When determining the compressive strength of the samples after 7, 28 and 90 days of curing, where W/B=const. and replacing 30% of cement by zeolitic waste, a low hydration activity and lower compressive strength in the initial period characteristic to pozzolanic reaction has been observed. Yet, after 90 days, the difference between compressive strength values is only 1.4%.

Cement replacement by zeolitic waste change the rheological properties of the concrete. It has been observed that when the amount of superplasticizer in the mixture is 2.0%, the slump flow of the mixture when increasing the amount of zeolitic waste slightly decreases, while when the amount of superplasticizer is 2.5%, increase of slump flow of the mixture has been registered. Slump flow of the concrete without zeolitic waste additive is 70cm, and with 30% of additive ~ 79cm.

Complex effect of zeolitic waste and steel fiber on slump flow of the mixture has been negative, although, this decrease of slump flow of the mixture has been determined by increased amount of steel fiber as opposed to increase of the amount of zeolitic waste in the mixture. Tendency of increasing slump flow of the mixture from 70 to 79cm has been observed in mixtures without steel fiber with concentration of superplasticizer being 2.5% and when increasing the amount of zeolitic waste (from 0 to 30%). Meanwhile, decrease of slump flow of the mixture from 63 to 60cm in the mixtures containing 25kg/m³ of steel fiber has been observed. Therefore, it can be mentioned that no facts of segregation was found in all SCC mixes by using tree cylinder method test.

Replacing higher amount of cement by zeolitic waste in the mixture changes the viscosity of the system. When the amount of steel fiber in the mixture is 25kg/m³, and increasing the amount of zeolitic waste from 0 to 30%, the time-span of slump flow t500 has increased from 1.16sec. to 3.72sec.

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**REFERENCES**


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**Fig. 14 The flow time t500 of the mixture dependency on the amount of zeolitic waste and fiber**
930-937.


