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Additives in Sorel Cement Based Materials - Impact Study

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Abstract: The subject of the research is the effect of micro-silica and polypropylene fibre additives on the physical and mechanical properties of composite materials ('concrete') made using oxychloride magnesium (Sorel) cement. The research aimed to improve the durability of the materials by incorporating these additives. The work shows the effects of these additives on compressive strength, corrosion and waterproofing properties. The addition of micro-silica was found to improve compressive strength by ~17.5% and to reduce water absorption. The addition of polypropylene appeared to increase compressive strength but only within the measurement uncertainties and also reduced water absorption. An additive concentration of x 10 the optimum polypropylene caused a ~x 4 reduction in compressive strength.

Keywords: Sorel Cement, Materials properties, Micro silica, Polypropylene fibres

1. Introduction

Significant industrial development has been achieved through the introduction of new solutions for the use of other materials added to concrete to improve its properties. Complying with the needs of modern Europe the use of industrial waste is increasing to reduce environmental pollution and in recent years this has been the subject of extensive research work. Additive materials from waste affect concrete's mechanical properties and thus can contribute to useful waste disposal.

Sorel cement-based materials with new additions have become the focus of research. The addition of polypropylene fibres to Sorel cement significantly affects the reduction of shrinkage cracks and micro cracks (Bensted 1989). The use of additives is a simple way of minimizing water absorption and permeability in Sorel cement. Additives can also reduce product penetration by chemicals that cause corrosion. This leads to many benefits for Sorel cement. Materials from this group have a high resistance to abrasion, compression and flexing and, with additives, exhibit greater resistance to water. Materials based on Sorel have good acoustic properties, significantly higher compressive strength and higher elasticity parameters (PN-EN 12390-5:2001). Such materials are resistant to oils and greases and have a fairly good resistance to road salt, sulphates, alkalis and organic solvents.

This research has improved the stability of products with Sorel cement by changing the microstructure. The work aimed to more strongly bind the magnesium ions in the oxychloride compounds occurring in the hardened cement and to achieve better packing by introduced into the mix micro-silica as an additive. In addition improvements in the mechanical properties of the materials were sought as a result of dispersed reinforcement. This has been achieved most frequently using steel fibres but also with other materials such as, for example, polypropylene.

In 1867, Stanislaw Sorel announced the development of oxychloride magnesium cement commonly called Sorel. This cement is prepared in situ by reacting an MgO (magnesium oxide) with an aqueous $MgCl_2$ (magnesium chloride) usually in the range of 20-30% concentration in water. MgO is obtained by decomposition through heating of magnesium carbonate:

$$MgCO_3 \rightarrow MgO + CO_2$$

Thus obtained, magnesium oxide is mixed with a solution of magnesium chloride containing at least 20% $MgCl_2$ in water. Along with heat generation, the mixture reacts to form a hardened product called magnesium oxychloride containing hydrated magnesium hydroxide to which is attributed a simple formula of Mg (OH) Cl.

It is formed by reacting:

$$MgO + MgCl_2 + H_2O \rightarrow 2Mg(OH)Cl$$

Mature cements are composed of magnesium hydroxide particles, the hexagonal phase of varying sizes, which grows a large quantity of fine needle crystals of oxychloride connecting together the material. The product is hard and has good strength, but is not resistant to the long-term damaging effects of water.

Sorel cements have been used for flooring and as a binding material. Cement surfaces were secured against water by polishing wax with turpentine.

Additives can affect the properties and quality of mortars as well as basic materials such as cement, gypsum or aggregates. They are widely used in various types of construction products to improve their technology and to ensure applicability under different conditions. Common additives are fluxes, sealants, air entraining agents, waterproofing and anti-foaming agents. The use of various additives, for example re-dispersible powders (ester of ethinyl acetic acid) and other organic compounds made up of polymers, has important influence on the properties of the obtained cement and has become the subject of many studies.

2. Additives Used in the Work

2. 1. Polypropylene Fibres

Chopped fibres (Deng 2003) of pure polypropylene are chemically inert and can generate hydrophilic effects ensuring ease of wetting contact with water in the concrete mix. The addition of polypropylene fibres to concrete mixtures causes reduction of shrinkage cracks and micro-cracks due to the settling of plasticisers, eliminates the need for steel mesh, reduces water absorption and water permeability, limits penetration of concrete by chemical substances, limits corrosion of concrete and reinforcing steel, increases frost and abrasion resistance, increases compression and flexural strengths by more than 10% to increase toughness and resistance to crushing, improves consistency and uniformity of concrete, increases workability and resistance to segregation of ingredients and increases the durability of concrete and reinforced concrete.

The fibres formed in the concrete mix comprise a spatial grid, which acts as a micro wire mesh preventing contraction. Elimination of shrinkage cracks in the concrete improves the tightness and reduces penetration to protect concrete structural reinforcement against corrosion. It also prevents aging of concrete and increases frost resistance.

The addition of polypropylene fibres for concrete improves the homogeneity. Concrete with fibres uniformly distributed in the mass retains the mixing water in the whole volume of the mixture by reducing the gravity fall of heavier components and excessive outflow of water which takes the form of a milky solution on the surface of the concrete element. This property of the fibres increases the strength of the surface at very high temperature. You do not need special care to prevent cracking of the concrete surface due to excessive evaporation of water but the surface region of the concrete mix stays moist for a long time until setting. Polypropylene fibres uniformly distributed throughout the mass of concrete limit segregation of the ingredients in the mix and prevent the formation of air voids. Concrete with fibre is more resistant to abrasion. Also fibre increases by 10% concrete tensile strength in bending and 14% in compressive strength. Fibre concrete has the ability to self-support and not breaks at cracks and, therefore, may be used in pre-fabrication with increased resistance to damage during transport and handling. The stabilizing effect of polypropylene fibres makes them useful in the repair of reinforced concrete structures, e.g. gunning.

Fibres can be added to concrete before or during mixing but the best effect is obtained by adding polypropylene fibres during the mixing of the gravel, sand and water to form an aggregate but prior to adding the cement. Mixing concrete with fibre for 5 minutes at 12 rotation/minute guarantees their uniform distribution. Polypropylene fibres can also be added to ready mix concrete in the mixer. The concrete should be mixed for at least 5 minutes. The recommended amount of fibre per 1 m^3 of concrete is 0.6-0.9 kg. Changing the proportions of the other ingredients is not necessary. Concrete with polypropylene fibres do not require any special handling or treatments other than the routine required by the Polish Standard and the surfaces of fibre concrete elements can be aligned and trowelled using conventional tools designed for this purpose.

2. 2. Microsilica

Micro-silica (Jasiczak, Mikołajczak 2003) is produced as waste in the steel industry and in the production of metal silicon, ferrosilicon and other alloys as a result of the reduction of high-purity quartz by carbon arc-resistance furnaces in continuous operation. The quartz evaporates as SiO and is re-oxidized to SiO_2 by contact with oxygen in the cooler parts of the furnace as the amorphous form of silica and condensed in the form of microscopic particles with grain size of approximately 0.1 mm.

The formation of silica dust can be summarized by the following reactions:

$$\mathrm{SiO_2 + C \rightarrow SiO + CO}$$

$$\mathrm{2SiO \rightarrow Si + SiO_2}$$

$$\mathrm{3SiO + CO \rightarrow SiC + 2SiO_2}$$

The amount of SiO_2 in the dusts output by these processes increases in proportion to the amount of silicon in the melt. For instance, ferrosilicon alloys containing 50% or 75% silicon have respectively 61 - 77% and 84- 88% silica dust and the metal silicon has up to 98% silica in the dust.

Initially, the interest in silica dust stemmed mainly from considerations of environmental protection and savings by replacing part of cement with this waste material. The usefulness of micro-silica in concrete technology found its practical reflection a quarter of a century ago. In 1971, structural concrete made in the mill Fisk in Norway used silica fume. In the same year the company "Sika Chemie" received the first patent for micro-silica and super plasticizers as cement additives. The first projects using silica fume concrete production in the United States and Canada took place in the early 1980s. Interest in the subject of micro-silica dust is constantly increasing as an attractive material for use in concrete especially in the era of super plasticizers to allow their dosage to be increased. The result of this cooperation is concrete with high durability and strength.

In Poland micro-silica is available as a dry particulate or as colloidal silica being an aqueous suspension of air and silica with or without additives. To complete the picture it should be added that there are other forms of micro-silica but they are not widely used in construction, for example silica granules, silica slurry and clumped silica dust.

3. Research on the Properties of Sorel Cement-Based Materials

3. 1. Compressive Strength

This test checks the maximum compressive stress sustainable by the concrete. It is critical in concrete design. This research was carried out on samples of cubic dimensions 150x150x150 mm^3. The preparation of concrete samples for testing was based on PN-EN12390-2 (Robinson & Waggman 1909). Polypropylene fibres of 19 mm characteristic length were used throughout. Concrete mix was immediately placed in the mould on a vibrating table. Excess cement above the upper edge of the mould was removed using two steel trowels. The test samples were clearly and permanently marked. The samples were taken out of moulds not earlier than 16 hours and not later than three days, protecting them from shock and loss of water. The samples were stored at ambient conditions being temperature of (20 ± 2) °C and relative humidity of ≥ 95% after removing from the mould.

Compressive strength testing was performed after 28 days of setting. The moist samples were dried and placed in a testing machine on a platen. Cubic samples were adjusted so that the load was applied perpendicularly to the direction of moulding. The increase in tension was between 0.2 to 1.0 MPa/s. The stress continued until destruction of the samples. The highest load to destruction was noted.

The compressive strength was calculated from the formula:

$$f_c = \frac{F}{A_c} \qquad [MPa] \qquad (1)$$

F - maximum destructive force [kN]

A_c - cross-sectional area of the sample experiencing the compressive force [m^2].

According to DIN EN 206-1 (PN-EN 206-1: 2003) on the basis of compressive strength values the strength of the Sorel cement-based materials can be determined as shown in Table 1 and Figure 1:

Table 1: Results of Compressive Strength Tests

COMPRESSIVE STRENGTH - DICE 150x150x150 [mm3]			
Material	**COMPOSITION OF SAMPLE**	**Destructive Force [kN]**	**COMPRESSIVE STRENGTH [MPa]**
Sorel Cement (PURE)	MgO 6720 g MgCl2 3033 g H2O 2660 ml Sand (0-2 mm) 9492 g Gravel(2-8 mm)14240 g zinc fluorosilicate 8,6 ml	226,1	10,05
		215,5	9,58
		222,4	9,88
Sorel Cement with POLYPROPYLENE FIBER (Non-optimum concentration x 10 of recommended)	MgO 4320 g MgCL2 1950g H2O 2750 ml Sand(0-2mm) 7120g Gravel (2-8mm) 10680g polypropylene fibres 66.8g zinc fluorosilicate 8.6 ml	61	2,71
		57,7	2,56
		47,7	2,12
Sorel Cement with MICROSILICA	MgO 4320 g MgCL2 1950g	243,3	10,81
		287,4	12,77

	H2O 1500 ml Sand(0-2mm) 7120g Gravel (2-8mm) 10680g microsilica 62.7g zinc fluorosilicate 8.6 ml	250	11,11
Sorel Cement with POLYPROPYLENE FIBER (at recommended concentration)	MgO 4320 g MgCL2 1950g H2O 2750 ml Sand(0-2mm) 7120g Gravel (2-8mm) 10680g polypropylene fibres 6.6g zinc fluorosilicate 8.6 ml	232,56	10,8
		213,18	9,99
		234,71	10,9

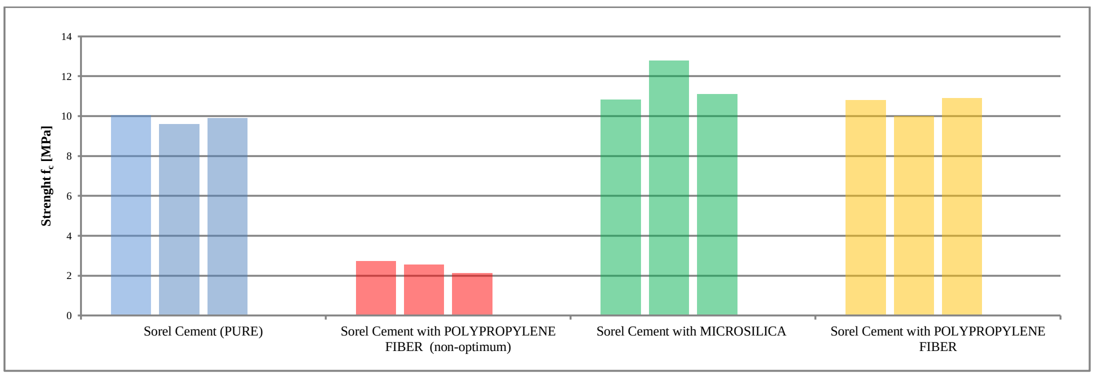

Figure1: Chart of compressive strengths vs. material composition

The addition of the micro-silica increases the compressive strength by 1.7 MPa being 17.5% of the ‘pure’ (no additive) material while addition of the polypropylene increases the compressive strength by 0.72 MPa within the uncertainties of the measurements.

3. 2. Examination of Water-Tightness

Water resistance was tested on samples of the same dimensions as previously. The water at the surface of the sample had a diameter of 100 mm and the time to exhaust the water reservoir through penetration of the concrete was measured. Table 2 comprises the water penetration data:

Table 2: Water penetration of Sorel cement-based materials – Exhaustion of water reservoir vs. Time

WATERTIGHTNESS		
Material	COMPOSITION OF SAMPLE	Water Penetration by Time
Sorel Cement (PURE)	MgO 6720 g MgCl2 3033 g H2O 2660 ml Sand (0-2 mm) 9492 g Gravel (2-8 mm) 14240 g	24 hours

	zinc fluorosilicate 8,6 ml	
Sorel Cement with POLYPROPYLENE FIBER (non-optimum)	MgO 4320 g MgCL2 1950g H2O 2750 ml Sand(0-2mm) 7120g Gravel (2-8mm) 10680g polypropylene fibres 66.8g zinc fluorosilicate 8.6 ml	48 hours
Sorel Cement with MICROSILICA	MgO 4320 g MgCL2 1950g H2O 1500 ml Sand(0-2mm) 7120g Gravel (2-8mm) 10680g microsilica 62.7g zinc fluorosilicate 8.6 ml	48 hours

3. 3. Corrosion

The rate of chemical corrosion processes depends on the materials and environmental conditions including:

- The chemical composition of the binder - cement (Portland cement, steel, aluminium) and aggregate (aggregate, limestone, compact, porous)
- Concrete structure (loose, dense, porous)
- Age of concrete: There is an optimum in terms of corrosion resistance as a function of concrete age. Young concrete is susceptible to leaching action due to incomplete hardening of the binder and a high content of calcium hydroxide while old concrete is susceptible to corrosion due to high porosity. Old concrete, however, is largely carbonated and thus less prone to leaching.
- Chemical composition and concentration of the environment as well as its state of matter (gas, liquid, aggressive solids) and the dynamics of change (change in concentration, flow and environment). The higher the rate of change of the higher rate of corrosion.

3. 3. 1. Acid Corrosion - a Solution of 5% HCl

Table 3 and Figure 2 presents the results of accelerated corrosion tests of samples exposed to a solution of 5% HCl:

Table 3: Results of acid corrosion tests (5% HCl)

MATERIAL	SAMPLE	INITIAL WEIGHT [g]	WEIGHT AFTER 24h [g]	WEIGHT LOSS AFTER 24h[%]	WEIGHT AFTER 7 DAYS [g]	WEIGHT LOSS AFTER 7 DAYS [%]
Sorel Cement (PURE)	MgO 6720 g MgCl2 3033 g H2O 2660 ml Sand (0-2 mm) 9492 g Gravel (2-8 mm) 14240 g zinc fluorosilicate 8,6 ml	808,28	696,64	-13,81	695,57	-13,94
		792,43	702,48	-11,35	701,38	-11,49
		877,23	791,43	-9,78	790,3	-9,91
with POLYPROPYLENE FIBER (non-	MgO 4320 g MgCL2 1950g	930,69	852,07	-8,45	851,5	-8,51

	H2O 2750 ml Sand(0-2mm) 7120g Gravel (2-8mm) 10680g polypropylene fibers 66.8g zinc fluorosilicate 8.6 ml	770,74	700,61	-9,01	698,93	-9,32
		775,51	689,48	-11,09	687,62	-11,33
Sorel Cement with MICROSILICA	MgO 4320 g MgCL2 1950g H2O 1500 ml Sand(0-2mm) 7120g Gravel (2-8mm) 10680g microsilica 62.7g zinc fluorosilicate 8.6 ml	762,3	656,41	-13,89	656,04	-13,96
		735,36	664,07	-9,69	643,93	-12,43
		746,27	661,84	-11,31	662,48	-11,23

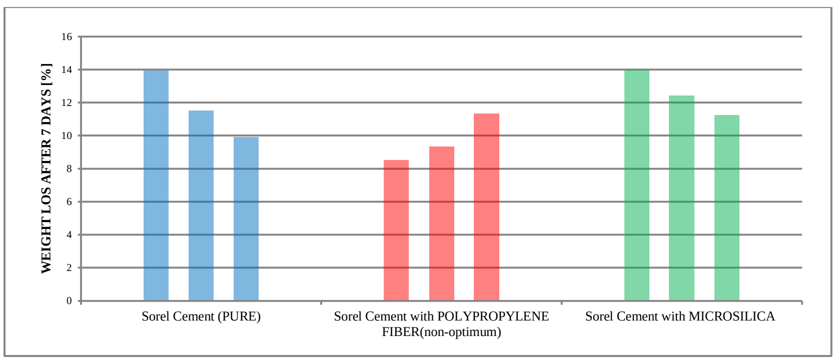

Figure 2: Chart of changes in weight after exposure to solution of 5% HCl

3. 3. 2. Corrosion - 15% Solution of Road Salt

Table 4 and Figure 3 presents data on samples of Sorel cement based materials in an environment of road salt and the resulting corrosion. The composition of the 15% solution of road salt is 15% NaCl, sulphates SO_4 (maximum of 3%), anti-conglomeration agent $K_4(FeCN)_6$ = 40 mg/kg, moisture content up to 3%.

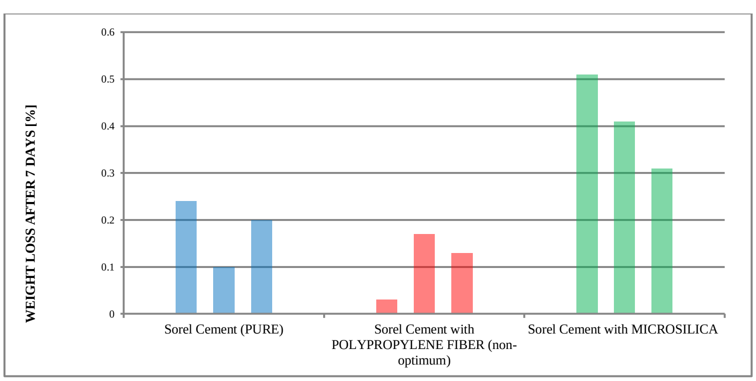

Figure 3: Chart of mass change in samples exposed to 15% solution of road salt

Table 4: Results of corrosion tests in a 15% solution of road salt

MATERIAL	SAMPLE	INITIAL WEIGHT [g]	WEIGHT AFTER 24h [g]	WEIGHT LOSS AFTER 24h[%]	WEIGHT AFTER 7 DAYS [g]	WEIGHT CHANGE AFTER 7 DAYS [%]
Sorel Cement (PURE)	MgO 6720 g MgCl2 3033 g H2O 2660 ml Sand (0-2 mm) 9492 g Gravel (2-8 mm) 14240 g zinc fluorosilicate 8,6 ml	823,73	825,74	0,24	825,28	0,19
		822,05	822,88	0,1	823,08	0,12
		854,48	856,17	0,2	856,23	0,2
Sorel Cement with POLYPROPYLENE FIBER (non-optimum)	MgO 4320 g MgCL2 1950g H2O 2750 ml Sand(0-2mm) 7120g Gravel (2-8mm) 10680g polypropylene fibers 66.8g zinc fluorosilicate 8.6 ml	911,49	911,78	0,03	912,48	0,11
		846,18	847,64	0,17	848,5	0,27
		829,62	830,66	0,13	831,18	0,19
Sorel Cement with MICROSILICA	MgO 4320 g MgCL2 1950g H2O 1500 ml Sand(0-2mm) 7120g Gravel (2-8mm) 10680g microsilica 62.7g zinc fluorosilicate 8.6 ml	715,69	719,34	0,51	723,04	1,03
		730,45	733,46	0,41	736,31	0,8
		760,46	762,83	0,31	766	0,73

4. Conclusion

The use of additives in the form of micro-silica and polypropylene fibres significantly alters the properties of Sorel cement-based materials.

Micro-silica added to Sorel cement confers new properties to the material strength and beneficially affects performance parameters of the material. The addition increases the compressive strength by 1.7 MPa being 17.5% of the ‘pure’ (no additive) material and reduces water absorption. The fine particles of micro-silica are applied to the matrix target material to fill the voids between the aggregates. They reduce the mixing water content in the binder and increase the density.

The addition of polypropylene fibres significantly reduces shrinkage cracks and micro cracks. Studies of water-tightness confirmed that Sorel cement has poor water resistance. Both micro-silica and polypropylene fibres were shown to reduce water absorption and permeability of the material, the reduced penetration likely to significantly limit corrosion. It is not recommended, however, to use more fibre than the determined optimum as use of large amounts of polypropylene fibres (19 mm characteristic length) in order to make better use of waste did not yield positive results. Here a ten-fold increase in the concentration of fibres in the material led to a ~4-fold reduction in its strength (Figure 1).

Sodium chloride induced corrosion causes a decrease in durability and strength of concrete through loss of material due to chemical leaching. It also causes weight gain due to the penetration and builds up of chloride salt crystals on the surface of the binder and in the pores of the material. In essence, in terms of mass we have two competing mechanisms – mass loss through erosion of cement materials vs. mass gain from formation of interstitial crystals of NaCl. We hypothesise that the significantly larger mass gain by the micro-silica added Sorel exposed to salt corrosion is due to reduced mass reduction through material loss, i.e. reduced corrosion.

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