

The Experimental Research on Special Polymerized Sulfur Composite-Impregnated Concrete and Cement Mortar

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Abstract

Specific chemical environments step out in the industry objects. This paper presents experimental investigation results of the chemical resistance of special polymerized sulfur composite impregnated concrete and cement mortar. The special polymerized sulfur composite applied as the industrial waste material.

The process of special polymerized sulfur composite as the industrial waste material production is a thermal treatment process in the temperature of about 150-155°C. The result of such treatment is special sulfur composite in a liquid state. Special sulfur composite in a liquid state is mixed with previously heated extender. In the paper there is presented development of the special polymerized sulfur composite as the industrial waste material, along with the practical uses in building industry. Also this paper presents the results of the experimental research and analyses indicating the usefulness of special polymerized sulfur composite to the protection against corrosion of concrete and cement mortar.

In this paper the review of the literature have been done, among other things about select using special polymerized sulfur composite in buildings, about the methods of the surface protection against corrosion of concrete and about the methods of the evaluation of protection layer on these materials. Also in paper presents materials also the domain of the personal investigations and the methodology are definite.

The research has comprised the compositions and the conditions for the formation of materials. The physical and mechanical properties of special polymerized sulfur composite have been evaluated.

After the analysis of the initial results the optimum compositions have been chosen to the experimental research. In this paper the usefulness of special polymerized sulfur composite to the surface protection against corrosion of the concrete and cement mortar have been evaluated.

Special polymerized sulfur composite impregnation of lean concrete and cement mortar increases its compressive strength from less than 1/3 to 1-1/2 times that of high strength concrete. Maximum absorption of special polymerized sulfur composite is achieved by carrying out the impregnation in molten sulfur under vacuum. Recent work indicates that satisfactory impregnation levels may also be achieved without the use of vacuum. Studies also show that while impregnation of high strength concrete and cement mortar increases its final strength to a value higher than that of low strength concrete, the relative increase in strength and the amount of special polymerized sulfur composite absorbed are smaller. Special polymerized sulfur composite impregnated concrete and cement mortar (SIC) may be used where high strength, resistance to water penetration, chemicals etc. are required. Available impregnating technology is applicable to precast concrete and cement mortar structures, while suitable technology for impregnating cast-in-place concrete needs to be developed.

The impregnation of building materials such as blocks and bricks with melted special polymerized sulfur composite increases the compressive strength by a factor of 2 and modulus of elasticity by a factor of 3. The permeability of special polymerized sulfur composite impregnated materials to water and salt solutions is also greatly reduced. Due to the large surplus of sulphur and the low price, special polymerized sulfur composite impregnation of building materials will find extensive use in tall building construction.

The space in concrete and cement mortar resulting from porosity reduces strength, exposes the concrete to chemical attack and, if filled with water, leads to destructive frost action at low temperatures. Filling the pores permanently and completely with an inert solid appears to be an effective way to improve mechanical properties and durability. Laboratory studies of impregnation with polymers have indicated that this is beneficial.

New developments in concrete and cement mortar special sulfur polymer materials have declined in the Poland. There are still many products that are widely used, but the growth of these materials seems to have stabilized. A brief summary of new products related to special sulfur polymer composite impregnation, repair, overlays and precast polymer concrete will be presented. Sulfur polymer composite impregnation, which has received little attention in recent years, currently has some very interesting applications. Repair materials, particularly low modulus sulfur polymer concretes, have proven to be very effective. An innovative overlay for use in areas where freezing and thawing is prevalent has been developed.

Keywords: Recycling; Chemical properties; Corrosion; Mechanical properties; Physical properties; Special polymerized sulfur composite

Introduction

Corrosion is a major problem from the social, economic, technical and scientific points of view. Despite extensive research and numerous papers on this subject, the problem has not been completely solved yet. It is estimated that in highly developed countries losses due to corrosion annually amount to about a thousand dollars per capita. In Poland they are estimated at 5-11% of the GDP, concern global economy [1-8].

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Corrosion contributes to the shortening of the service life of building structures, i.e. to a reduction in their capability to perform the required functions over a given period of time [9-15].

Corrosion affects practically all building materials, not only steel, concrete or reinforced concrete (of course, no building material, structural element or building is everlasting). Generally speaking, the fight against corrosion comes down to providing a given material or element with protection whereby its failure free service life is significantly extended [16-21].

In order to demonstrate the suitability of special polymerized sulfur applied as the industrial waste material for the surface protection of concrete and cement mortar experimental research was carried out in the Institute of Building Engineering at Wrocław University of Technology [22-34].

Properties of the elementary sulfur have been known for years. In the articles [1,35-41], they are already precisely described.

In the paper presents the personal investigations and the methodology for special polymerized sulfur - impregnated concrete and cement mortar applied as the industrial waste material to industries objects. After the analysis of the initial results the optimum special polymerized sulfur compositions have been chosen for the experimental research in the industries objects [1,35-41].

Some specific environments with varied corrosivity occur in industries objects. Soil with varied composition, structure and corrosivity, chemical relationships and chemical substances, organic environment of industries buildings, and the atmosphere of industries objects manufacturing plant protectives and fertilizers are among the most significant [42-51].

As far as construction made of reinforced concrete is concerned the corrosivity of industries building environment is much higher than that typical for rural one and it may be compared to that of atmosphere of chemical industry [52-58].

It depends on humidity and on concentration of compounds which make electrical conductivity of the condensate to increase and react chemically (battle chemicals and the battle relationship) with after that they have dissolved in it [59-66].

There are several ways possible of protecting ferroconcrete industries constructions: pre-galvanizing steel, using alloy steel, cathodic protection, electrochemical extraction of chlorides, re-alkalizing carbonated concrete. Protective coating, if needed, can be used to prevent corrosion of reinforcing steel, e.g. when concrete lagging may not to be tight, too thin or none, on connecting parts of precast concrete units. Special polymerized sulfur – impregnated concrete and cement mortar applied as the industrial waste material may be an example.

Experimental research of concretes and cement mortars impregnated with special polymerized sulfur applied as the industrial waste material has been attempted [67,68].

In paper presents the personal experimental investigations and the methodology for special polymerized sulfur – impregnated concrete and cement mortar applied as the industrial waste material to industries objects.

At ambient temperature special sulfur applied as the industrial waste material crystallizes in the rhombic system (α -S). It melts at the temperature 105-110°C and crystallizes from this melt to the form of

β -S (monocyclic) which changes again to the α -S at 95-96°C as discussed elsewhere [64,65].

Melted sulfur polymerizes applied as the industrial waste material in the industries objects as discussed and published elsewhere [56-67]:

- 155-160°C it is brown and indicates increased viscosity,
- between 200 and 250°C it is dark brown with high viscosity value,
- 240-250°C depolymerization and diminishing of viscosity begins; at 400°C sulphur is very fluid,
- 443-444°C is the temperature of its boiling. The rapid process of cooling sulfur in water changes it from fluid state to an elastic-plastic body, brown-yellow coloured. In this state sulfur is composed of two different polymerized forms: S_λ (yellow) and S_μ (dark red-brown). S_μ has a higher molecular mass.

Sulfur may be obtained in the colloidal state as discussed elsewhere [56-67]:

- after boiling with water and $\text{Ca}(\text{OH})_2$ and precipitation with HCl-S_μ ,
- after hydrolysis of alcohol solution - S_λ .

From the chemical reactivity point of view, sulfur may be oxidised and as well easy reduced (it forms many sulphides and organo-sulphur compounds). Elementary sulfur finds rarely applications. It is used to the production of some kind of cement for special purposes, e.g. to join ceramics and metallic parts of electric insulators and in the industries objects. The mechanical properties of this cement are good (strength about 45-50 MPa by compression), and its chemical inertness is appreciated (in comparison to the Portland cement containing concretes). Sulfur is also used in dermatology as discussed elsewhere [1,33-35,68].

Functional properties of the special polymerized sulfur and sulfur polymer based products as discussed and published elsewhere [39-51]. Orthorhombic special polymerized sulfur is also subject to deterioration by bacteria, sunlight, very strong alkalies, and thermal fluctuations [1,33-35,68].

Samples and Methods

Special polymerized sulfur applied as the industrial waste material were investigated in two stages. In the first stage, compositions were fixed and thirty test special sulfur were prepared and pretested. The pretesting included preparing special polymerized sulfur and determining their basic physical and mechanical properties, such as: bulk density, absorbability by wt., bending strength and splitting tensile strength.

The special polymerized sulfur as the industrial waste material view of the Figure 1a and 1b. Special polymerized sulfur applied as the industrial waste material in the industries objects were investigated in two stages. In the first stage, compositions were fixed and thirty test special polymerized sulfur were prepared and pretested.

The compositions of the binder-sulphur applied as the industrial waste material: 97.86% S_8 , fine sulfur, oil: 2.13%, the ash: 0.01%, producer "Siarkopol" Tarnobrzeg. The special polymerized sulfur applied as the industrial waste material view of the Figures 1a, 1b and 2.

When fixing the compositions, the special polymerized sulfur: 97.86% S_8 , fine sulfur producer "Siarkopol" Tarnobrzeg. The pretesting

included preparing special polymerized sulfur and determining their basic physical and mechanical properties, such as: bulk density, absorbability by wt., bending strength and splitting tensile strength. The experimental results are reported in detail in [56-67].

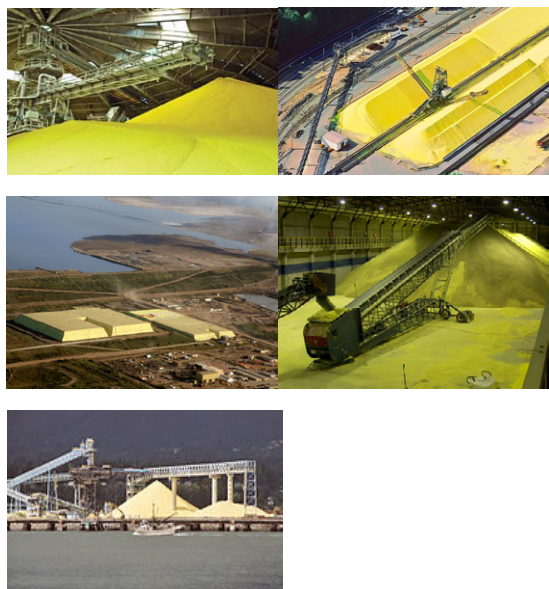


Figure 1a: A view of the special polymerized sulfur applied as the industrial waste material in Europe.

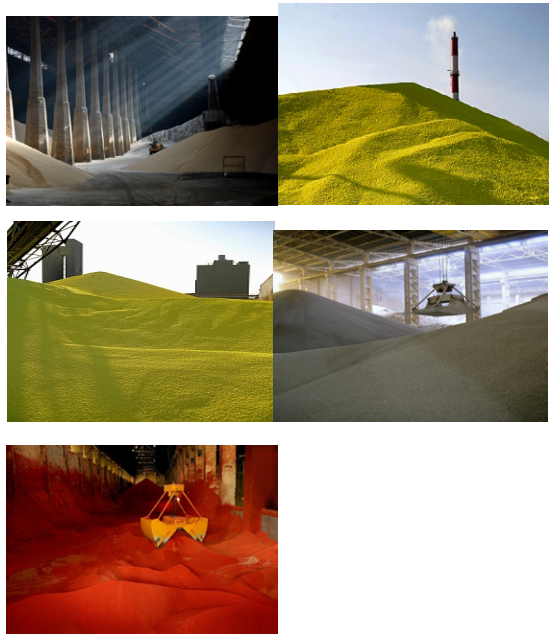


Figure 1b: A view of the special polymerized sulfur applied as the industrial waste material in Poland.

The results of the preliminary tests were analysed and the special polymerized sulfur in the industries objects having the best properties among the tested composites was selected for further studies. The basic information about the preparation of special polymerized sulfur is given in Table 1. The composition of the special polymerized sulfur applied as the industrial waste material in the industries objects is given in Table 2 and its experimentally determined properties are shown in Tables 3 and 4.

The special polymerized sulfur applied as the industrial waste material view of the Figure 2. Chemical element of the special polymerized sulfur applied as the industrial waste material view of the Figure 3.

Cylindrical samples 35 mm in diameter and 38 mm in height and 10×10×60 mm and 40×40×160 mm rectangular samples were used to determine apparent density ρ_{pm} and water absorption by weight n_{wm} of the polymer sulphur composite. 10×10×60 mm and 40×40×160 mm and 100×100×100 mm rectangular specimens were used to bending strength f_{dm} . Cylindrical samples 35 mm in diameter and 38 mm in height were used to determine tensile splitting strength $f_{ct,sp}$. Cylindrical samples 35 mm in diameter and 38 mm in height and 10×10×60 mm and 40×40×160 mm and 100×100×100 mm rectangular specimens were used to determine compressive strength $f_{cm,c}$. 10×10×60 mm and 40×40×160 mm rectangular samples were used to determine longitudinal modulus of flexural elasticity E_{dm} while cylindrical samples 35 mm in diameter and 38 mm and 40×40×160 mm in height were used to determine longitudinal modulus of compressive elasticity E_{cm} .

It was prepared by melting special polymerized sulfur at the temperature 150-160°C and then by cooling to the ambient temperature [56-67].

Impregnation Technique: The samples were immersed for 5-20 min. and remaining specimens for 0.5 hours in molten special polymerized sulfur. The specimens were then removed from the steel vessel, and excess liquid sulphur on the surface was wiped off. The samples were cooled in water for 20 minutes in order to crystallize the sulfur in the surface pores and prevent loss of sulphur by evaporation, and were then left at room temperature to cool in the air. The specimens were weighed before and after impregnation and sulfur loading calculated. The impregnated specimens look shiny greenish to dark grey depending upon the original color of the specimens. However the rough texture is not very much affected. The total process time is 0.20-0.30 hours (20-30 min) for samples. The samples concrete and cement mortar impregnated special polymerized sulfur binder applied as the industrial waste material view of the Figure 4.

Investigation Results

The viscosity of special polymerized sulfur as a function of temperature applied as the industrial waste material view of the Figure 5.

In 2008-2014 author reported on research with special polymerized sulfur - infiltrated concrete and cement mortar and noted that special sulfur has economic advantages over organic polymer. When the impregnation was vacuum assisted, an exceedingly strong and durable concretes and cement mortars could be produced by precasting.

Binder	Temperature of the polymerization composite [°C]	Time of the polymerization composite [min]	Time of coagulation of composite [min]
1	2	3	4
special polymerized sulfur	150-160	40-60	15-30

Table 1: Basic information about the preparation of special polymerized sulfur.

Content in [%] of total composite mass		
Binder	Filler	Additive
1	2	3
Sulfur S ₈	Mineral quartz dust	Carbon black
[%]	[%]	[%]
100	-	-

Table 2: Composition of the special polymerized sulfur applied as the industrial waste material in the industries objects.

Average bulk density ρ_{pm} [g/cm ³]	Average absorptability by wt. n_{wm} [%]	Average bending strength f_{dm} [MPa]	Average splitting tensile strength $f_{cl,sp}$ [MPa]	Average compressive strength f_{cmc} [MPa]	Coefficient of fragility k [-]	Coefficient of direct elasticity E_{dm} under bending [GPa]	Coefficient of direct elasticity E_{cm} under compression [GPa]
2.00	0.01-0.02	<u>10.0</u> 5.8%	<u>3.0</u> 7.2%	<u>50.0</u> 8.5%	0.90	60	65

Note: the percentages under the line are coefficients of variation.

Table 3: Experimentally determined properties of special polymerized sulfur applied as the industrial waste material in the industries objects.

Properties	Unit	Requirements	Test methods according to:
Thickness of the impregnation	mm	from 0,2 to 0,6	acc. to the technical sheets of the manufacturer
Coat's adhesion to concrete*)	MPa	>1,0	PN-EN 1542:2000
Diffusion resistance for steam*)	m	<1,2	PN-EN ISO 7783:2001
Diffusion resistance for carbon dioxide*)	m	>50	Test procedure ITB Nr LO-6
Water penetration coefficient*)	kg/(m ² h ^{0,5})	<0,1	PN-EN 1062-3
Resistance to action of 150 cycles of freezing and defrosting in water and NaCl solution*)	-	no changes in the coat	IBDiM Test Procedure No. SO-3 Visual valuation
Coat's adhesion to concrete after testing frost resistance as above *)	MPa	>1,0	IBDiM test procedure No. SO-3 PN-EN 1542:2000

* for coats 1.0-1.5 mm thick

Table 4: Characteristics of special polymerized sulfur composites – impregnated concrete and cement mortar applied as the industrial waste material in the industries objects.

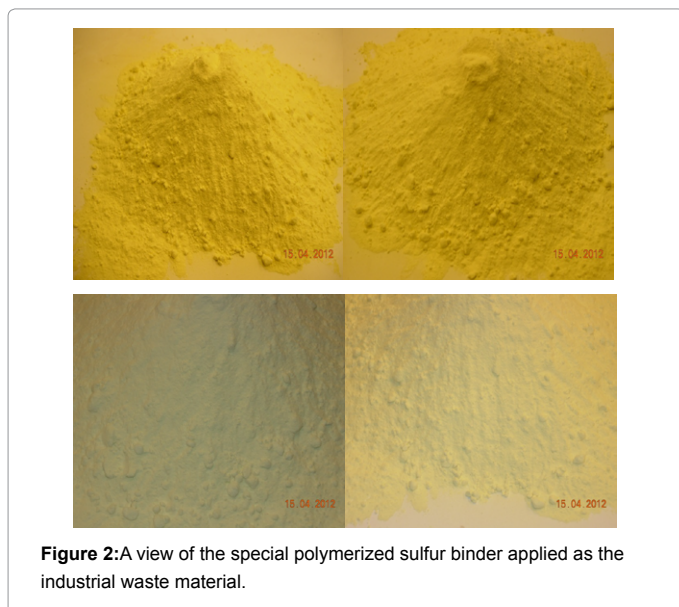


Figure 2: A view of the special polymerized sulfur binder applied as the industrial waste material.

Author did not recommend his particular formulation for cast-in-place use. In effect, the special sulfur was used as a substitute for some of the Poland cement, because the concrete and cement mortar, being infiltrated, had a water-cement (w/c) ratio of 0.70 about 4.0 bag/yd³. In 2008-2014 it was concluded that at least in Poland this infiltrated concrete and cement mortar would probably be less costly than Poland cement concrete having a w/c of 0.40. The sulfur-infiltrated concrete had a compressive strength of over 0,000 lb./in. 2 (700 kg/cm²), withstood 200 cycles of freezing and thawing without damage, and

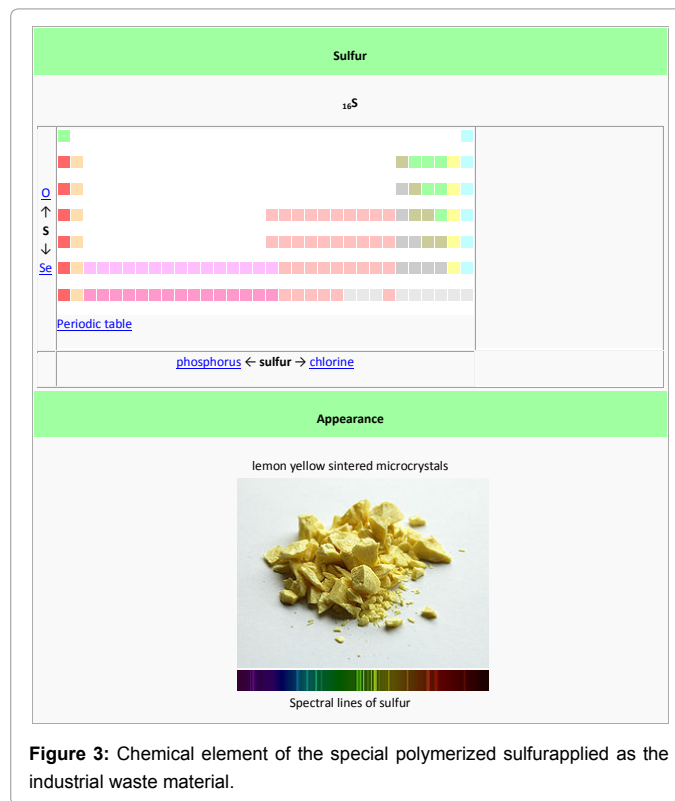


Figure 3: Chemical element of the special polymerized sulfur applied as the industrial waste material.

was exceedingly resistant to chemical attack. Apparently, the special polymerized sulfur fills the capillaries and prevents absorption of water



Figure 4: A view of the samples concrete and cement mortar impregnated special polymerized sulfur binder applied as the industrial waste material. A view natural surface of ordinary cement mortar and concrete impregnated special polymerized sulfur composite applied as the industrial waste material.

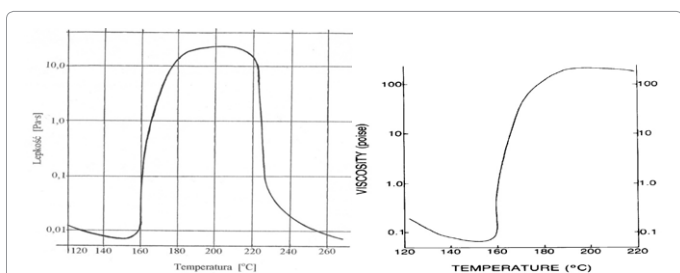


Figure 5: Viscosity of special polymerized sulfur as a function of temperature.

or chemicals and this prevents the critical saturation that causes freeze-thaw distress. A personal communication from author indicated that there had been no change in the properties of this laboratory concrete in five years.

The tremendous increase in properties was offset by the complexities of the impregnation process: drying to remove all of the moisture, evacuating the air, applying the special polymerized sulfur under pressure to fully impregnate the concrete, and the application of heat or irradiation to fully polymerize the monomer. To fully impregnate large precast components such as several city collectors, bridge girders, bridge deck slabs, piling, and wall panels would require a large, efficient facility that would be difficult to justify unless it could be shown that a market for a large volume of PIC products would be forthcoming. No such facility has ever been developed in the Poland. Until some breakthroughs in process technology are realized, there is little likelihood that fully-impregnated PIC members will ever become economically feasible. This is unfortunate since PIC has such exceptional strength and durability properties.

A view of the municipal collector's sewer impregnated special polymerized sulfur applied as the industrial waste material is presented in Figure 6. The view of studied concretes samples was showed on Figure 7. The Composition of cement concretes of city sewer collector's impregnated special polymerized sulfur is presented in Table 5.

Research was also successful in developing processes for partial depth impregnation that could be used in the field for impregnating bridge decks and other concrete and cement mortar surfaces. The process required drying the concrete to remove moisture from the surface, applying the special polymerized sulfur on a thin sand layer that held the special polymerized sulfur during the time the monomer



Figure 6: A view of municipal collector's sewers. The city sewer collectors were impregnated special polymerized sulfur applied as industrial waste materials.



Figure 7: A view of concrete samples. The concrete samples were impregnated special polymerized sulfur applied as industrial waste materials.

Cement concrete constituent materials [kg/m ³]	C30/37 (B37)
Aggregate 0-2 mm	760
Aggregate 2-8 mm	332
Aggregate 8-16 mm	674
CEM I 32,5R	372
Water	212
w/c	0.57

Table 5: The composition of just concretes of city sewer collectors impregnated special polymerized sulfur.

was being imbibed into the concrete, and then polymerizing the monomer using steam heat. The process was capable of producing impregnated depths of 10 to 60 mm. The concrete surfaces were much more resistant to water absorption, had much higher abrasion resistant, and in generally were much more durable. The downside was that the process normally took about one day and subjected the concrete to high temperatures during drying that resulted in micro cracking, and was rather cumbersome. Many bridge decks in the Poland were successfully impregnated during the 1980-1985, but the development of polymer concrete overlays provided a simpler, faster and less costly method for waterproofing concrete surfaces.

More recently, however, there has been a successful commercial application of partial depth impregnation. The special polymerized sulfur vacuum impregnation system uses a plastic membrane that is applied over the surface of a slab, statue, column or wall and vacuum to evacuate the air from the pores.

Summary and Conclusion

It can be concluded from the test results that the tested special polymerized sulfur composite can provide surface corrosion protection in concrete and cement mortar. Special polymerized sulfur composite has not been applied for this purpose before. The tests have shown that a proper thickness of the special polymerized sulfur composite and the type of surrounding corrosion environment are important factors here.

The test results presented in this paper and discussed elsewhere indicate that the special polymerized sulfur composite – impregnated concrete and cement mortar applied as the industrial waste material can provide surface protection against corrosion for concrete. Special polymerized sulfur composites have not been used for this purpose before.

The authors are aware that although the range of the tests carried out so far is quite wide, still further tests are needed to ultimately determine the suitability of the special polymerized sulfur composite for the surface protection of the concrete and cement mortar against corrosion. Also a simple and practical technology of applying this material (polymer) to the surface of concrete and cement mortar needs to be developed.

The tests carried out in the Institute of Building Engineering at Wrocław University of Technology, although quite extensive, have not exhausted the full range of experiments to which the investigated special polymerized sulfur composite should be subjected in order to have complete certainty that it can provide effective surface protection against corrosion for concrete and cement mortar. Also a simple and fast technology of applying the composite to the surface of concrete in building practice needs to be developed also tests in temperatures below 0°C and < 0°C (-10 ÷ -20°C) inclusive allotropy and influence on fire protection.

The process of special polymerized sulfur composite applied as the industrial waste material production is a thermal treatment process in the temperature of about 150-155°C. The result of such treatment is special polymerized sulfur composite in a liquid state.

Special polymerized sulfur in a liquid state is mixed with previously heated extender. In the paper there is presented development of the special polymerized sulfur composites as the industrial waste material, along with the practical uses in building industry.

The test results presented in this paper indicate that the special polymerized sulfur composite can provide surface protection against

corrosion for concrete and cement mortar. Special polymerized sulfur composite have not been used for this purpose before.

Recent research has led to the development of durable special polymerized sulfur mortars, concretes, and coatings. All of the methods of using special polymerized sulfur as a binder for rigid concrete rely on the reaction of one or more modifiers to stabilize, in the hardened state, at least a portion of the special polymerized sulfur in its less brittle, less dense form. The durability of the concrete produced appears to depend on the modifying system used. In all cases the special polymerized sulfur must be heated to a liquid state to react with the modifier and to mix with and coat the aggregate and filler.

Special polymerized sulfur – impregnated concrete and cement mortar can develop high strength, attains strength in 0.5 hours, requires no special curing, resists acids and organic liquids, has no known undesirable reactions with aggregates, and requires no limitation on the ambient temperature at the time of placement. When its use becomes economically feasible, concrete impregnated special polymerized sulfur will be an excellent material for use in pavement repairs and bridge deck overlays.

Solidified impregnate in the small pores of solids are normally in metastable equilibrium. Spatial restrictions prohibit the formation of regular crystal habit. Because of the formation of non-crystalline modifications the free energy is increased. In addition, owing to the large surface-to-volume ratio the surface-free energy is also large. In the absence of concave menisci or strong interaction with the matrix that would reduce the energy, the tendency for spontaneous exudation from the pores is increased.

Special polymerized sulfur - does not interact strongly with siliceous surfaces, so that water or other liquids can penetrate the porous network and adsorb on the substrate surface, weakening further the interaction between it and sulfur. Water adsorbs also on sulfur, creating a lubricating effect and high stresses due to surface energy decrease. Both effects facilitate extrusion and the latter cause's destruction.

Because of the relatively slow penetration of water, non - isotropic expansion creates strains beyond the elastic limits. Impregnated porous solids of small size can be successfully utilized for predicting the behavior of large sized systems.

It is recommended that any further data collection by the Research Council include on-site inspection of placements and interviews with highway department people involved. It is recommended that any steps towards the widespread utilization of special polymerized sulfur in Poland await the results of research on the use of it as a patching material, a bridge deck overlay, or in other applications. The Research Council should remain alert to any developments in this field. Unless detailed instructions for the mixing and placing of special polymerized sulfur impregnated concrete become available, it will probably be necessary for the first sizable Poland placement of this material to be made by a contractor experienced in its use. Such a placement should be made with Poland and Russia aggregates and probably in a zone having a severe climate.

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