PUBLISHER :

Address of Publisher
& Editor's Office :
GDAŃSK UNIVERSITY
OF TECHNOLOGY
Faculty
of Ocean Engineering
& Ship Technology
ul. Narutowicza 11/12
80-952 Gdańsk, POLAND
tel.: +48 58 347 13 66
fax : +48 58 341 13 66
e-mail : office.pmr@pg.gda.pl

Account number :
BANK ZACHODNI WBK S.A.
I Oddział w Gdańsku
41 1090 1098 0000 0000 0901 5569

Editorial Staff :
Kazimierz Kempa Editor in Chief
e-mail : kkempa@pg.gda.pl
Przemysław Wierzchowski Scientific Editor
e-mail : e.wierzchowski@chello.pl
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e-mail : janmi@pg.gda.pl
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Piotr Bzura Managing Editor
e-mail : pbzura@pg.gda.pl
Cezary Spigarski Computer Design
e-mail : biuro@oficynamorska.pl

Domestic price :
single issue : 20 zł
Prices for abroad :
single issue :
- in Europe EURO 15
- overseas US$ 20

Special Issue 2008
published by:
www.oficynamorska.pl

ISSN 1233-2585

POLISH
MARITIME
RESEARCH

in internet
www.bg.pg.gda.pl/pmr/pmr.php

POLISH MARITIME RESEARCH
Special Issue 2008

CONTENTS

The papers published in this issue have been reviewed by :
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Editorial

POLISH MARITIME RESEARCH is a scientific journal of worldwide circulation. The journal appears as a quarterly four times a year. The first issue of it was published in September 1994. Its main aim is to present original, innovative scientific ideas and Research & Development achievements in the field of :

Engineering, **Computing & Technology**, **Mechanical Engineering**,

which could find applications in the broad domain of maritime economy. Hence there are published papers which concern methods of the designing, manufacturing and operating processes of such technical objects and devices as : ships, port equipment, ocean engineering units, underwater vehicles and equipment as well as harbour facilities, with accounting for marine environment protection.
The Editors of POLISH MARITIME RESEARCH make also efforts to present problems dealing with education of engineers and scientific and teaching personnel. As a rule, the basic papers are supplemented by information on conferences , important scientific events as well as cooperation in carrying out international scientific research projects.

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Project Eureka E!3614
on
Advanced coating of interior of tanks for rising environmental safety of tankers
CORET

COATING OF INTERIOR OF SHIP FUEL TANK – AN ALTERNATIVE FOR RISING ENVIRONMENTAL SAFETY

Message of the project's coordinator

This is the special issue of the Polish Maritime Research quarterly, focused on aspects of basic features and application problems of a new philosophy for environmental protection of ship hull fuel tanks, consisting in the additional coating of tank shell structure . The new idea - instead of the "classical" design based on single shell plating - introduces the second , additional semi-elastic fuel oil barrier consisted of polyurethane coating supported on passive or active lightweight - concrete core layer. This was the aim of the EU-supported EUREKA project - CORET. The project was focused on the following aspects:

- *selection of a material for the inner layer with taking into account such its properties as: resistance to reaction with adjacent cargo, fire resistance, electrostatic, mechanical and technological properties, ageing problem, etc*
- *modelling of the rock penetration process in the case of grounding the tanker, with a view of determining the properties, span and dimensions of the inner coat layer (especially capability of developing plastic deformations), as well as the properties of the core material*
- *problems of technology of application both the coating and core material to base steel structure of various configurations*
- *maintenance problems of so modified structure, esp. problems of its inspection*
- *problems of recycling and utilisation of used materials.*

Papers presented in this issue are based on results of the research programmes carried out within the frame of the project in question.

Janusz Kozak, The Project's Coordinator

Chief executor and coordinator of the project:

Gdańsk University of Technology
Faculty of Ocean Engineering and Ship Technology

Gdańsk 2008

POLISH MARITIME RESEARCH Special Issue 2008; pp. 4-7
DOI: 10.2478/v10012-007-0069-y

Elastic protection coatings for ship fuel tanks, intended for the increasing of environment protection level

Janusz Kozak
Gdansk University of Technology

ABSTRACT

Small closed sea shipping regions (such as the Baltic Sea) are specially vulnerable to consequences of ecological disasters due to spills of fuel oil used for ship propulsion and carried in single-plating double-bottom tanks. An alternative solution (against the recommended double- plating structure) was proposed. It consists in applying the second, elastic protection barrier to decrease risk of oil spills resulting from loss of tightness of ship plating in consequence of e.g. collision or grounding.

Keywords : elastic protection coatings, ship tanks, environment protection

INTRODUCTION

Dramatic increase of amount of cargo shipped by sea and associated increase of number of cargo ships, observed in the world fleet for several last years, has been mainly caused by progressing process of economy globalization. For this reason many sea regions of the world have become more busy and hazardous for navigation. Small closed navigation regions are specially endangered by possible sea disasters. One of them is the Baltic Sea [1]. On average about 2000 ships every day sail in this waters, Fig. 1.

These are ships of different types; out of the total number of 13600 ships crossing Skagen between July 2005 and October 2005, 60% of them belonged to dry cargo ships, 25% - tankers, 7% - passenger ships and 8% - other ships [2]. Main shipping routes in the Baltic are presented in Fig. 2.

Moreover, a further dynamic increase of number of cargo ships sailing in the Baltic waters is predicted - Fig. 3 [2].

The Baltic Sea basin is a specific region of the world not only due to the busy shipping routes. It is a sea of a very limited amount of water exchanged with the ocean – the time necessary to completely exchange its water with the Atlantic Ocean is estimated to be 25÷30 years, which means that in the case of a greater oil spill in the region its consequences will be severe and long-lasting. According to the performed analyses [3] the probable profit loss resulting from tourism limitation in a spill suffering region would be many times greater than pollution removal cost. Additionally, in the Baltic waters – apart from shipping routes – in coastal zones are also carried out other activities such as fishing, tourism and operation of farms of wind power plants.

The very intensive ship traffic over the restricted area of the Baltic greatly influences occurrence number of sea accidents.

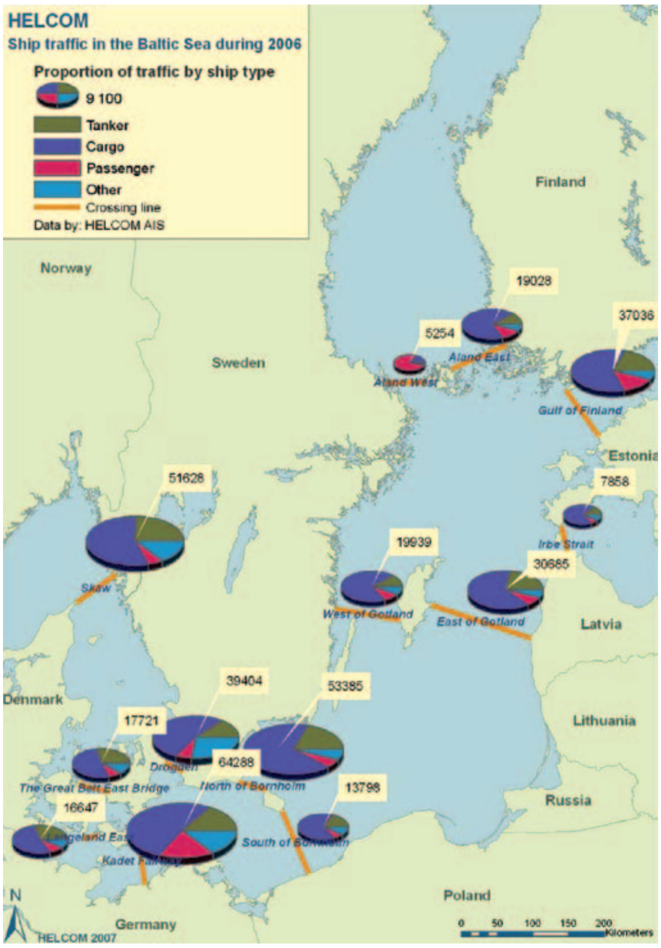

Fig. 1. *Ship traffic in the Baltic Sea [2]*

Fig. 2. Main shipping routes in the Baltic Sea [3]

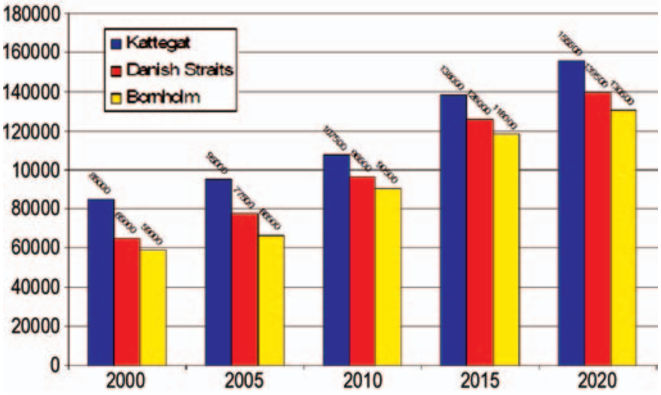

Fig. 3. Ship traffic intensity (ships/year) in the Baltic [4]

The high traffic intensity, difficulty in navigation through the straits leading from the North Sea to the Baltic, often occurring bad weather conditions and other factors make that the Baltic is a sea region where many ship accidents occur year by year. The highest number of 146 sea accidents was recorded in 2005; as many as 13 of which resulted in pollution of the environment [4].

The map of particular kinds of the accidents together with indication of places of their occurrence is presented in Fig. 4.

In the years 2000-2006 the most frequent cause of ship accidents was grounding (46%), the next one - ship-to-ship collisions (31%). A failure of ship power plant or structure was responsible for disasters in 3% cases, and fire - in 5%. The most severe accidents which caused oil spills in the Baltic are listed in Tab. 1.

***Tab. 1.** The most severe pollutions caused by spills of oil product materials from ships in the Baltic waters [6]*

Year	Ship name	Amount of spilled oil	Place
2003	Fu Shan Hai	1200 t	Bornholm (Denmark/Sweden)
2001	Baltic Carrier	2700 t	Kadetrenden (Denmark)
1998	Nunki	100 m^3	Fjord Kalundborg (Denmark)
1995	Hual Trooper	180 t	Sund (Sweden)
1990	Volgoneft	1000 t	Karlskrona (Sweden)

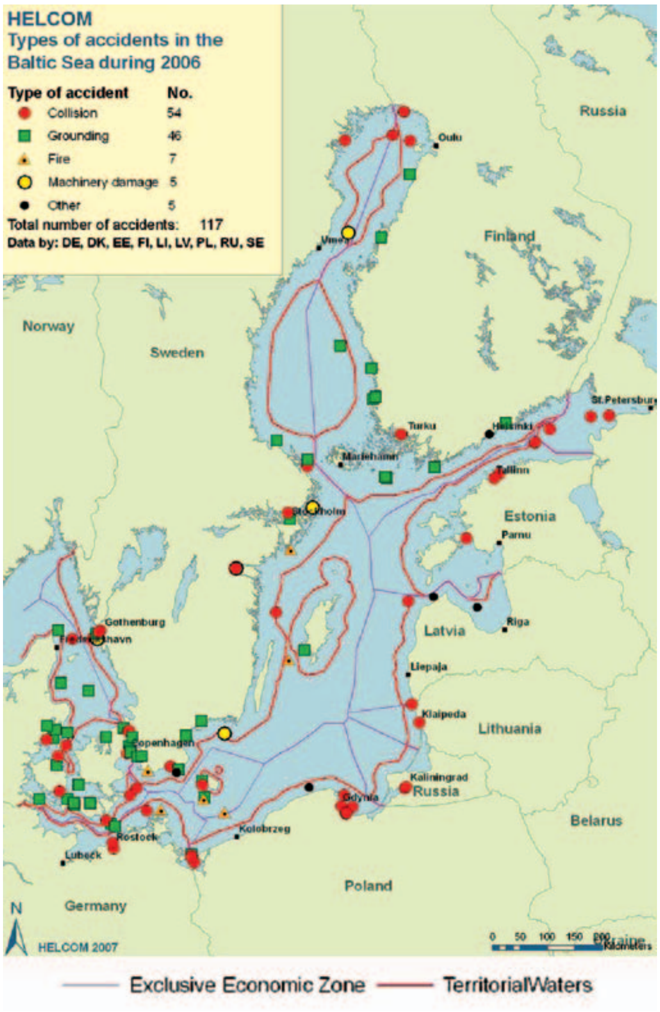

Fig. 4. Places where ship accidents occurred at the Baltic Sea in 2006 [5]

In the connection with the increasing risk of ecological disasters associated with sea transport, in the last years the European Union adopted two packages of legal instruments dealing with safety at sea, the so called principles: *Erika I* and *Erika II*. As a result of their implementation the range of port control of ships was intensified and extended, and single side plating ships were banned from oil shipping; also, the European Maritime Safety Agency (EMSA) was established. In 2005 the European Commission prepared the package *Erika III*.

In the existing and being- in- force requirements for construction and equipment of new ships possible collisions and groundings have not been taken into account. Only basic design regulations concerning stability and floatability of damaged ships or amount of spill of liquid load from damaged hull are commonly adopted. However in 2004 Germanischer Lloyd (GL) introduced to its rules the notation COLL which determines degree of ship hull resistance (strength) against collisions [7]. The resistance is measured by comparing the strength against impact of strengthened ship side structure with that not strengthened of single plating. The only regulations directly concerning collisions are the requirements for ships intended for inland navigation on the Rhine (Switzerland, Germany, the Netherlands), introduced in 2003. The ADNR regulations require to so design structural elements of gas tankers as to make them able to absorb the energy of 22 MJ released during collision against ship side structure [8].

Though for cargo tanks of oil cargo tankers the legal requirements have been recently made much more stringent, similar ones for fuel oil tanks are still lacking, nevertheless amount of fuel oil contained in them is often comparable with that of liquid cargo carried by a small tanker. The hazard becomes greater by the fact that most of such tanks is located in double bottom, i.e. in the zone very susceptible to failure both in the case of ship-to-ship collision and the taking of ground or rock.

IDEA OF THE PROGRAMME CORET

The above mentioned premises indicate that grounding or collision of e.g. a container carrier of medium size may lead to environmental pollution of the Baltic by the oil released from unseal single plating bottom tanks and its amount can be significant. In this connection was undertaken a research work aimed at elaboration of a way of lowering the risk of releasing oil spill in the case of collision, by introducing a second protection barrier. The idea of the project consists in adding an internal elastic oil-resisting coating placed inside the tank on a foundation which fills the tank in such a way as to ensure – in the case of tank plating tear occurring as a result of a collision - tightness of the tank by means of the elastic coating able to be displaced to some distance and thus to prevent against oil spill in emergency, Fig. 5.

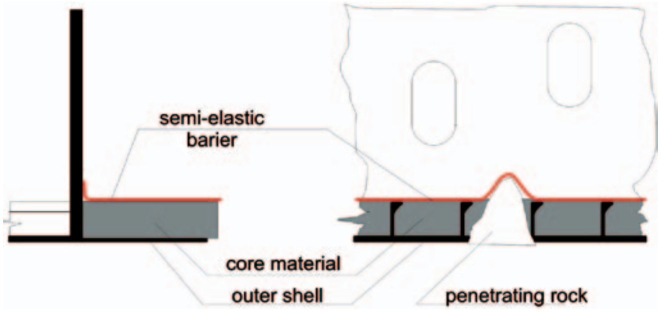

Fig. 5. *Idea of the second elastic barrier for fuel oil bottom tank.*

In order to elaborate such novel solution many problems should be first investigated including the following:

- elaboration of recipe for an oil resistant plastic material, inexpensive and suitable for coating it inside closed spaces in shipyard's conditions.
- selection of a material for intermediate filling layer,
- elaboration of an engineering process of applying the components of the barrier in industrial conditions with special taking into account difficult places such as corners, bends etc,
- selection of the dimensions of the second barrier components: depth of the filling layer and thickness of the protection coating,
- influence of the additional coating and filling material on corrosion rate of steel structure,
- elaboration of a method for control of state of hidden surfaces,
- making agreement with classification societies as to principles of implementation and use of the novel solution.

The mentioned problems constitute the subject of work carried out in the frame of the research project EUREKA E!3614 „CORET": *"Elastic protection coatings for ship tanks to increase environment protection level "*. Below are presented results of a preliminary work associated with developing some of the above mentioned problems.

SELECTION OF A FILLING MATERIAL INTENDED FOR SUPPORTING THE SECOND BARRIER

During searching for a filling material for supporting the elastic internal barrier, was performed a comprehensive research study to select materials which satisfy majority of a dozen or so requirements, often contradictory to each other. Such filling material should be light in weight, non-flammable, non-gassing in an elevated temperature, non-toxic, non-corrosive, easy for implementing in industrial conditions, easily utilized and inexpensive, of course. After reviewing possibly applicable materials it was revealed that lightweight concretes can fulfill most of the postulated features. The concretes are of the volumetric density not greater than 2000 kg/m^3 in dry state. In land structures they are used to significantly lower weight of an element and/or its dimensions. The concretes are made by mixing cement mortar and various natural or artificial aggregates. Application of lightweight aggregates makes it possible to obtain the concretes of the strength exceeding 60 MPa, at simultaneous reduction of structural weight by 25÷30% relative to the common concrete. It leads to a significant reduction of cost of shuttering, scaffolding and reinforcement, as well as to a reduction of dimensions of structural elements, thus - total volume of concrete, and to reaching a greater freedom of designing. The application of lightweight artificial aggregates to concretes results not only from the need of obtaining more lightweight structures but also from limited resources of rock aggregates and economic necessity of utilization of industrial wastes. This is especially important in the aspect of implementing the balanced development policy recommended by European Union.

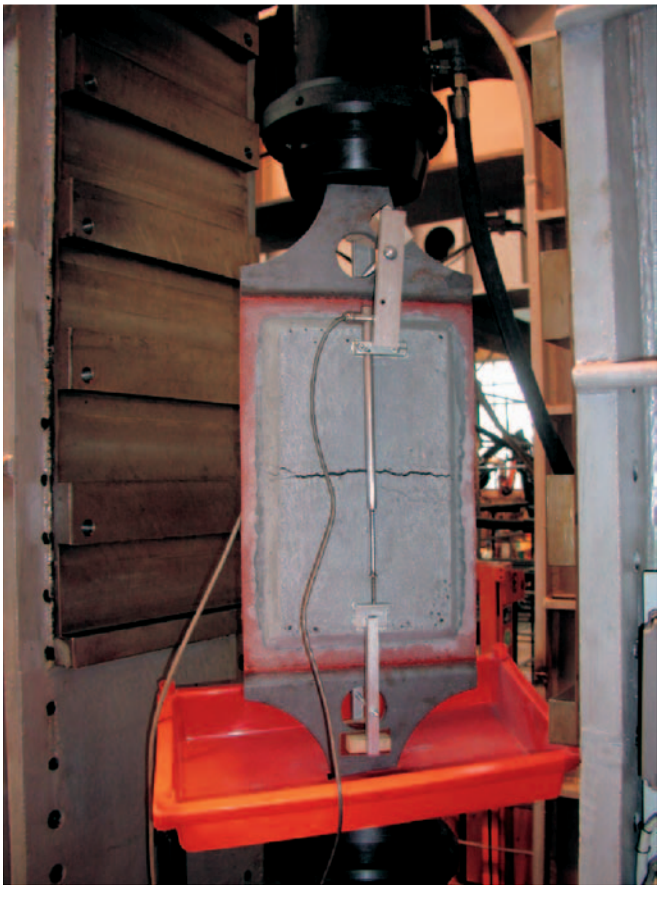

Fig. 6. *Tests of mechanical properties of filling layer*

A characteristic common feature of all lightweight aggregates is their porous structure and - as a rule - a lower strength than that of hardened cement mortar. Consequently, concretes made of the aggregates differ from common ones not only in their volumetric density but also other features as well as manufacturing process.

During the work on choice of parameters of concrete filling material, the laboratory tests of mechanical properties of various combinations of concrete and aggregate, and on applicable way of preparation of steel structure surface, were carried out by using full-scale specimens. In Fig. 6 is presented the specimen tested to determine a degree of binding the filling material with the steel structure under tension, depending on a way of preparation of steel plate surface, and in Fig. 7 – the example record of deformation of the concrete filling material versus deformation of the steel structure.

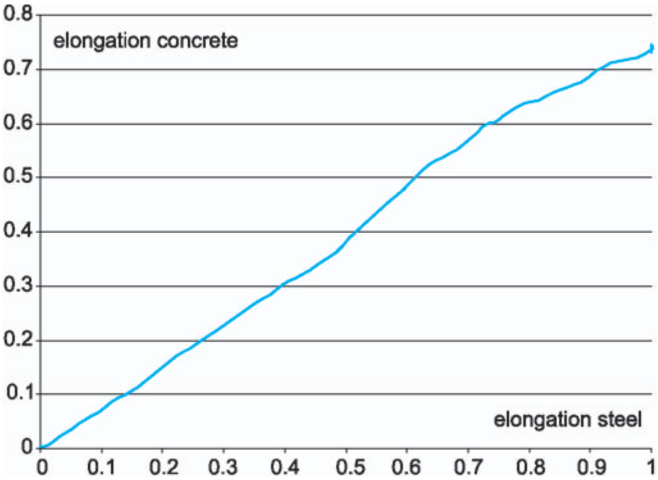

Fig. 7. *Relative elongation of concrete filling material versus elongation of deforming steel structure.*

SELECTION OF AN INTERMEDIATE LAYER BETWEEN THE CONCRETE FILLER AND 2ND BARRIER COATING

Concrete – especially lightweight one - is, after applying, a porous, fragile material which contains significant amount of water for a long time after forming. From the properties result problems of weak adhesion to smooth steel background, as well as of worsening the features of the 2nd barrier layer applied „in situ" because - as a result of the water released from the concrete - water vapour bubbles able to lower mechanical properties and tightness of applied layer of the 2nd protection barrier, appear. Therefore one of the tasks of the carried out project was devoted to the finding of solutions for the increasing of lightweight concrete adhesion to steel background as well as to the 2nd barrier layer so as to stop releasing the water contained in concrete, during application process of the 2nd barrier. The mentioned problems were solved by introducing an intermediate layer combined of epoxide resins and quartz sand [9]. Effectiveness of the solutions was checked by means of strength tests of the obtained concrete-coating connection by applying both the tensile test pieces – such as shown in Fig. 6, and the test of pull-off the coating from the background – in the way as in the case of paint coatings, Fig. 8.

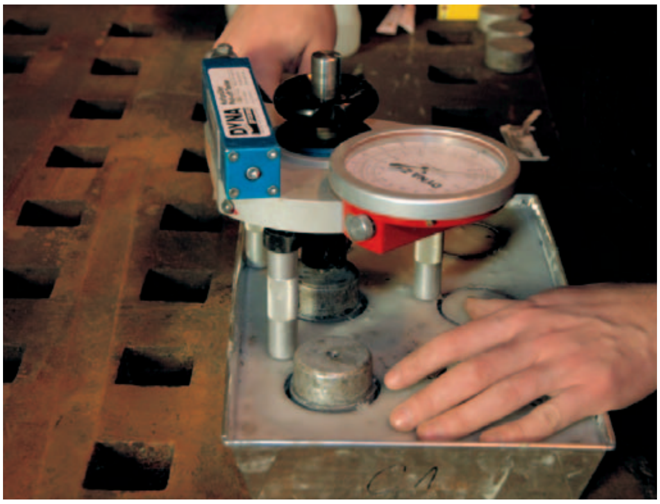

Fig. 8. *Measurements of adhesion of concrete filler to protective barrier*

SUMMARY

- Large number of cargo ships sailing over small, restricted water areas such as the Baltic Sea can endanger - in the case of disaster –the environment by spilling fuel oil carried in the ship's bottom tanks for ship propulsion.

- An alternative solution (against the double plating structure) was proposed consisting in applying the second, elastic protection barrier to decrease risk of oil spill resulting from loss of tightness of ship plating as a consequence of e.g. collision or grounding.

- Implementation of such solution would make it possible to increase safety of existing ships without necessity of their expensive rebuilding.

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POLISH MARITIME RESEARCH Special Issue 2008; pp. 8-13
DOI: 10.2478/v10012-007-0070-5

Advanced coating of interior of tanks for rising environmental safety - novel applications of polyurethanes

Janusz Datta
Józef T. Haponiuk
Gdańsk University of Technology

ABSTRACT

The aim of this study was to develop urethane elastomers of predefined properties to be used as elastic coating in the cargo tanks of tankers. A method for coating the liquid polyurethane system onto steel and steel-concrete elements, and a way to join polyurethane coating with the aforementioned elements, were elaborated. The technique of injection the reactive liquid polyurethane system onto cold steel elements was used. The method for utilization and recovery of urethane oligomerols from the waste polyurethane coating in chemical recycling by using low molecular weight glycols as glycolysis agents was proposed.

Keywords: polyurethane elastomers, multi-layer constructions, adhesives, recycling

INTRODUCTION

Urethane elastomers are polymeric materials which are used more and more often in industrial applications to solve particularly difficult problems. This is due to the fact that the segmented and domain structures of polyurethanes create a good combination of features such as elasticity, mechanical resistance and hardness. Cast urethane elastomers can be used as construction elements because these polymers are characterized by large modulus of elongation, tear strength, high abrasion resistance, good tensile properties as well as they display better load -carrying capacity than rubber elastomers. Moreover, they are resistant to the factors causing physical ageing (air, ozone) and also to the commonly used solvents, oils and weathering. Glass transition temperature (Tg) of rigid segments usually ranges from 107°C to over 200°C, while for flexible segments it depends on the oligomerol used and most often falls below –30°C. These features predispose polyurethanes to being used in products exposed to temperatures below and above 0°C [1]. The application of polyurethanes as a polymer core in the SPS (Sandwich Plate System) constructions in building of ships or drilling platforms is well known [2]. This particular technology has been approved for ship aplications by Lloyd's Register [3] and other recognized classification societies. SPS technology allows the elimination of large number of reinforcement features in steel elements which facilitates their production, reduces the number of welds and at the same time, eliminates the sources of fatigue cracks and corrosion. The other advantages are: a reduction of the construction weight and building costs (shorter time is necessary to produce construction elements); increased precision of production and construction longevity; lower labor consumption including troublesome welding and painting operations; a reduction of surfaces requiring anticorrosive protection; the facilitation of applying paints; and a significant reduction in the extent, time and costs of maintenance and repairs. An important advantage of sandwich systems is their high resistance to impact energy, capability of damping vibrations, good fire resistance, and thermal and acoustic insulation. The use of polyurethane systems of density more than six-fold lower as compared to steel, to the polymeric core production allows to obtain a light construction that is additionally reinforced within the whole double hull of the ship [1, 3].

Sandwich systems are made from steel sheets interlaminated with a layer of polyurethane. Steel-polyurethane composites have been widely applied in construction industry, e.g. to build bridges, where unusually large steel elements are used. SPS structures are lighter and less time-consuming to build than those made of steel, and they have an in-built fire and vibration resistance.

In the case of a road bridge constructed in Saint Martin de Beauce (Canada), the use of the steel-polyurethane sandwich system resulted in the bridge mass reduction of 60% as compared to the construction built with traditional technology. At present, steel-polyurethane building elements are used for constructing sports facilities, public and industrial buildings, storage facilities, drying houses, commercial cold stores, temporary facilities on the construction sites, containers, stores, freezers as well as office and apartment buildings.

The aim of our work was to develop a polyurethane elastomer of defined properties and the technology for coating it on large-size ship structures, and to obtain a hybrid steel-polyurethane-concrete sandwich system of defined mechanical resistance of joints.

EXPERIMENTAL PART

Materials

The following materials were applied: 4,4'- diphenylmethane diisocyanate (MDI), liquid, filter-purified, manufactured by Borsdochem (Hungary); oligo (oxytetramethylene) diol (PTMG) molecular mass 1000, manufactured by Du Pont (USA); oligo (oxypropylene) diol (ROKOPOL D2002) molecular mass 2000, manufactured by Inter Rokita S.A., Brzeg Dolny (Poland); oligo(ε - caprolactone)diol (CAPA 212) molecular mass 1000, manufactured by Solvay (Belgium);oligo (ethylene-butylene adipate) (POLES 55/20) molecular mass 2000, manufactured by Organika - Zachem S.A. (Poland); 1,4-diazabicyclo[2.2.2]octane (DABCO) manufactured by Hondry – Hüls (Germany); butylene glycol (BDO) manufactured by BASF (Germany); 1,6-hexanediol (HDO) manufactured by Du Pont, (USA);1,3-propanodiol, manufactured by POCh (Poland); ethylene glycol (GE), manufactured by POCh (Poland); oligo(oxyethylene)diol (PEG 300) manufactured by Aldrich-Chemie; orthophosphoric acid manufactured by POCh (Poland)

Catalysts: potassium acetate (KAc) manufactured by POCh, sodium hydroxide (NaOH) CIL bonding agents.

Measurements

The viscosity of prepolymers and glicolysates was measured with a Brookfield DV-II viscometer (manufactured by Brookfield Engineering Labs. INC. Stoughton, U.S.A.) equipped with a SP31 spindle.

The measurements were performed at 50, 60, 70 and 80°C for the spindle's rotational speed of 60rpm. The density values for prepolymers and glicolysates were determined picnometrically at 50°C. Density was calculated based on the mass of picnometer with glicolysate, empty picnometer and the picnometer filled with water.

Spectral analysis of prepolymers, glicolysates, urethane elastomers and polyurethanes obtained from glicolysates was performed by means of a Nicolet 8700 FTIR spectrometer (Thermo Electron Co.) by using the Specac Golden Gate single-reflection diamond-heated ATR accessory. Spectra were recorded at 4cm^{-1} resolution for 64 scans. Thermogravimetric analysis of polymer samples was conducted with a Netzsch TG 209 analyzer. Samples were heated from 20°C to 500°C at the rate of 10°C/min. The analyses were performed in an argon atmosphere. The values of $T_{5\%}$ and $T_{10\%}$ were read from thermograms, while the temperature of the fastest mass loss from the DTG curve. Gaseous products that originate during thermal decomposition of the analyzed samples were analyzed by means of a FTIR spectrometer coupled with the thermobalance. Based on the obtained spectra, the main decomposition products were identified and their emissions in dependence on temperature were compared. Dynamic mechanical thermal analysis was performed by means of a Mk III thermomechanical analyzer (Polymer Laboratory) by using the probe suited for up to 300°C, a temperature range from 25 to 120°C, the rate of temperature change of 4°C/min, and frequency 10 Hz. Samples of the approximate dimensions 10 x 50 x 3 mm were analyzed. Resistance- to- stretch measurements (modulus of rigidity and elongation) were determined according to PN - ISO 37: 1998 with a Zwick Z020 universal tensile machine in samples with the dimensions 80 × 10 × ca. 2mm. For each type of elastomer and polyurethane from recyclate, three samples were investigated. Resistance to abrasion was determined by means of a Schopper-Scholbach apparatus; samples shaped as truncated cones (3 for each material type) were cut with the in-built cutting device. The values of polyurethane density were measured with a Westphal-Mohr balance. Distilled water was used as an immersion fluid.

THE DEVELOPMENT OF URETHANE PREPOLYMERS

Urethane prepolymers were obtained in a reaction between di-isocyanide MDI and different oligomerols. To this end, the pre-calculated amount of an oligomerol was introduced into the heated reactor. Next, after drying and de-gassing of this ingredient at 60°C, liquid MDI devoid dimers and trimers was being added in the amount necessary to obtain - via chemical reaction - prepolymer of defined structure (content of NCO groups from 4 to 9%). After the reaction, prepolymer was stabilized with orthophosphoric acid [4-10]. Prepolymers were characterized by determining variation in the [NCO] group concentration and dynamic viscosity at different temperatures and shear stress values (Brookfield viscometer), and by an FTIR spectral analysis. Prepolymer density was measured picnometrically. Chemical stability determinations of prepolymers with different structures were conducted during 4 weeks.

THE DEVELOPMENT OF SANDWICH SYSTEM MATERIALS

Based on the obtained prepolymers, a technology for producing moulded urethane elastomers by means of the RIM technique was elaborated to suit defined properties of the material. Moulded urethane elastomers for using as elastic protective coating were obtained in this study by means of a two-step method. Step I consisted of prepolymer synthesis, while step II was the prepolymer elongation by means of BDO or GE glycol. The material to be used as urethane coating was obtained for different molar [NCO]:[OH] ratios ranging from 0.95 to 1.20. It has been established that for the ratio of 1.05 the material had the maximum hardness measured after 24h in warm samples. Polyurethane systems of various chemical compositions were also investigated with the aim to develop a way of joining the cross-linked polyurethane layers among themselves and with other materials. In this study a wide spectrum of factors was considered which might influence the joint strength such as polyurethane system temperature, the temperature and time of gelation, surface preparation and adhesive type. Experiments were conducted without an adhesive as well as with the previously selected glues, i.e. epoxy adhesive (patent KTP), Thixon 405 (ICI) and CILBOND (CIL).

RECYCLING OF ELASTIC POLYURETHANE COATING

Recycling of material was applied for the mass ratios of scrap polyurethane to glycol ranging from 2:1 to 10:1 [4-16]. A catalyst was used in the process. The reactor loaded with glycol and catalyst was heated at temperatures from 190 to 240°C. Dosing time varied and depended on the mass ratio of polyurethane to glycol. After the reaction, glycolysates were cooled down. The liquid products were poured into a vessel and left for 24h to allow phase separation. Polyurethanes were obtained from glycolysates by means of prepolymer method and using, as before, di-isocyanide MDI and different extenders [17,18].

RESEARCH RESULTS

PREPOLYMERS

Urethane prepolymers with the viscosity values from 1000 to 55000 mPas were developed in dependence on the [NCO] group concentration, temperature and shear stress. They were used as semi-products in the production of urethane elastomers to be applied as protective coating [10,19]. In Fig. 1 the variations of dynamic viscosity of urethane prepolymers obtained from Rokopol D 2002 and di-isocyanide MDI, in dependence on the rotation speed of the probe and prepolymer temperature, are presented. The FTIR spectra confirmed the time-dependent structural changes in prepolymers. In Fig. 2 the spectra of the 4-week old prepolymers obtained from Rokopol D–2002 and MDI, are shown.

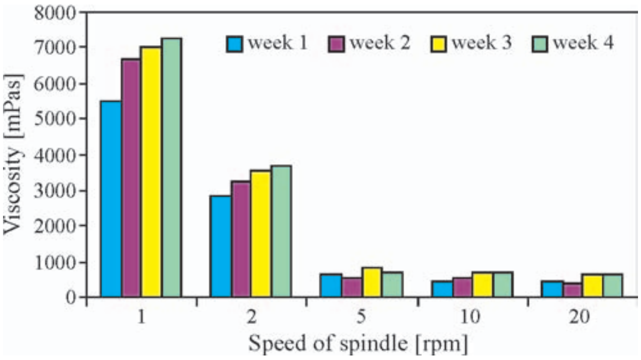

Fig. 1. *Relation between the number of revolutions of the spindle and dynamic viscosity of urethane prepolymers investigated over a period of 4 weeks. [NCO] = 6%; measurements performed at 75°C*

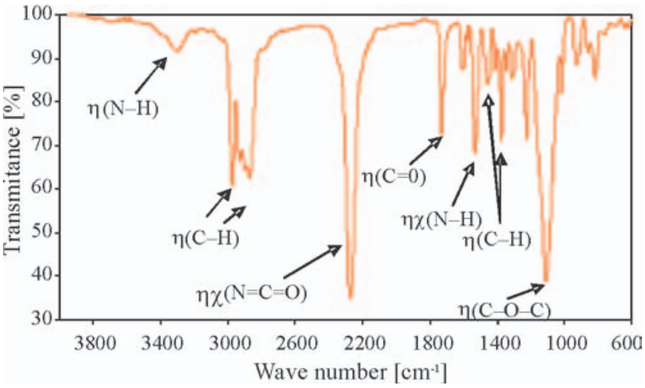

Fig. 2. *FTIR spectrum of prepolymer with the [NCO] group concentration of 7% (4 weeks after the synthesis)*

The obtained urethane prepolymers absorbed infrared light within the frequency range (600-4000 cm^{-1}). The resulting spectra were very similar and displayed, as predicted, the comparable infrared absorption bands for the identical frequency ranges. It has been observed that over the period of 4 weeks, the intensity of the NCO band at 2273 cm^{-1} was decreasing. This shows that the content of NCO groups in the prepolymer was decreasing, and therefore the prepolymer structure was changing. It has been determined that prepolymers obtained from PTMG were characterized by higher chemical stability as compared with those obtained from MDI and Rokopol D2002 (Fig. 3); the former displayed a small change of ca. 0.2% in the [NCO] group concentration while in the latter such concentration change reached as much as 12%. Prepolymers obtained from oligoestrols, i.e. Poles 55/20 had chemical stability similar to that of the prepolymers obtained from Rokopol D2002.

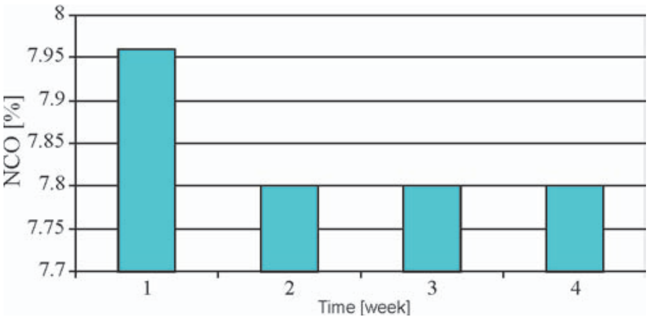

Fig. 3. *Variation of the [NCO] group concentration in urethane prepolymer obtained from MDI and PTMG over a period of 4 weeks. Initial [NCO] concentration=8%*

ELASTOMERS

Based on the analysis of the tangent of the loss angle in function of time (see Fig. 4), the glass transition temperature (T_g) was determined for the elastomers obtained from the previously developed prepolymers. (T_g) corresponds to the maximum on the tg δ = f (T) curve at which the transition between the glassy and rubbery state occurs. The glass transition temperatures measured by the DMTA method in polyurethanes produced with BDP extenders ranged from -2 to 5°C [11-14].

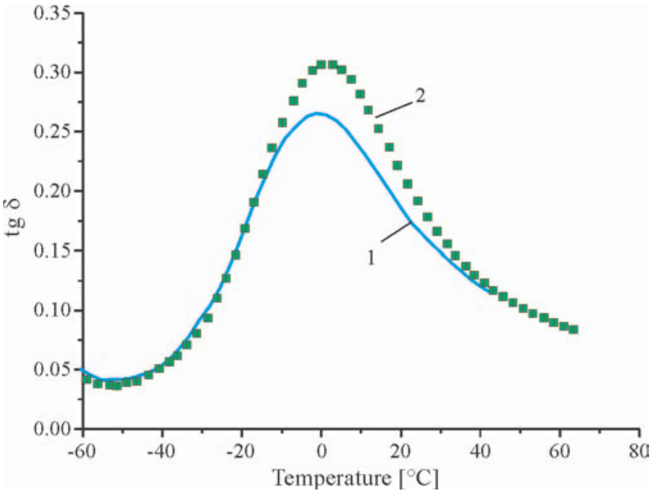

Fig. 4. *Temperature dependence of the loss tangent of PU obtained from MDI, PTMG and low molecular weight extender BDO for different molar [NCO]/[OH] ratios. Curve 1 - PU9P-1.00; curve 2 - PU10P-1.05*

The strength characteristics of the polyurethane used as elastic coating is shown in Fig. 5. The material was obtained by the RIM technique by means of pouring the polymer into steel moulds without pre-heating and without heat treatment during the gelation and cross-linking steps. The results of strength analysis performed on layered samples with different chemical structures are presented in Tab. 1, while the outcome of a study on the interaction between crude oil and the obtained polyurethane is shown in Tab. 2.

The capacity of the samples to absorb crude oil varied with the structure and propeties of specific polyurethanes. For the polyurethane obtained from Poles 55/20 ([NCO] = = 9 %; Tab. 2), Capa 212 and Poles 55/20 ([NCO] = 5 %), the capacity values ranged from 0.59 to 1.33 %, from 0.92 to 1.34 % and from 0.78 to 1.12 %, respectively. The absorbance capacity measurements were performed over a period of 364h.

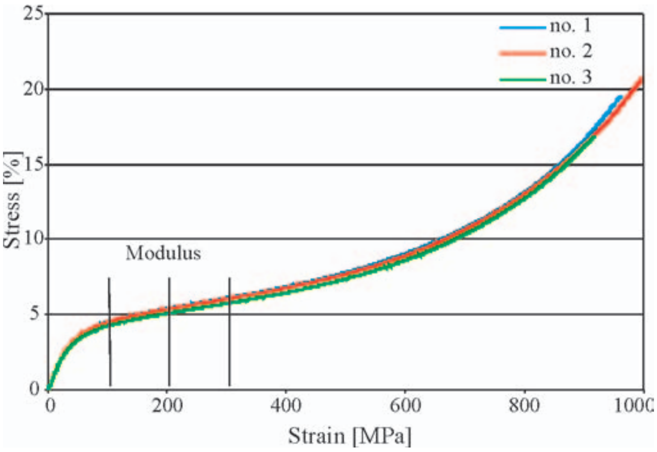

Fig. 5. *Stress-strain characteristics of polyurethane used as protective coating (3 samples)*

In order to define the conditions for obtaining strong jointing between the various polyurethane types and between polyurethanes and other materials, a number of layered samples were prepared that differed in the layer thickness and properties. Varied conditions were used to obtain the dual-layer samples, i.e. different temperatures of mould as well as of system, different levels of cross-linking of polymer before pouring onto it or jointing it with the second layer, and varying polymeric surface conditions.

Based on the obtained results, it has been established that the surface treatment of steel elements by grit blasting definitely improved the adhesion of polyurethanes to steel. The use of adhesives mostly increased the strength however in the case of large-size products the problem of applying the adhesive quickly enough had become apparent.

It was also determined that the production process of layered samples did influence the strength of polyurethane-steel joints [15, 16]. Samples obtained by pouring the urethane system between the metal elements were characterized by a higher strength than those obtained by gluing the cross-linked polyurethanes to steel sheets. This latter finding resulted in the choice of the RIM technique for applying polyurethane coating onto steel and steel-concrete constructions during our study.

HYBRID POLYURETHANE-STEEL-CONCRETE ELEMENTS

In this study the elastic polyurethane coating was applied into the fuel tanks in the form of liquid polyurethane system that was being dispensed onto the light ceramic material filling the steel construction. Preliminary experiments to verify this method were conducted by coating large-size steel samples covered with ceramic material of varying surface characteristics and water content. The polyurethane system was poured onto steel-concrete samples by using a EC305 machinery (Secmer, France). In the technology developed by us, the protective

Tab. 1. *Strength properties of polyurethane dual-layer samples with different structures. Prepolymer obtained from MDI + Poles 55/20 (samples PU1PC – PU6PC), and from MDI + Capa 212 (other samples). The NCO group concentration in polyurethane prepolymer ca. 9%*

Symbol of dual-layer sample	Modulus 100 [MPa]	Modulus 200 [MPa]	Modulus 300 [MPa]	Tensile strength [MPa]	Tensile elongation [%]	Permanent elongation [%]
PU1PC	11.0	14.7	17.6	20.3	520	36
PU2PC	11.0	14.3	16.6	25.1	544	41
PU3PC	11.2	12.8	14.4	15.0	340	32
PU4PC	12.3	15.2	18.3	23.8	400	40
PU5PC	11.1	14.0	16.9	20.0	421	30
PU6PC	11.0	12.6	14.4	22.7	448	36
PU7PC	10.1	12.6	14.9	18.4	336	22
PU8PC	13.2	14.5	17.7	19.1	387	28
PU9PC	12.6	13.1	14.3	15.2	416	28
PU10PC	10.0	11.7	12.9	17.9	440	36
PU11PC	10.5	11.6	11.8	12.4	320	22
PU12PC	11.3	12.8	13.3	13.6	360	27

Tab. 2. *Measurements of capacity for absorbing crude oil by single-layer polyurethanes obtained from MDI, Poles 55/20 and BDO. The NCO group concentration in polyurethane prepolymer ca. 9 %*

Sample symbol	Initial mass of dry sample [g]	Capacity for absorbing crude oil [%]									
		24h	48h	72h	96h	168h	192h	216h	250h	274h	346h
PU1P9	2.0008	0.23	0.27	0.35	0.39	0.52	0.56	0.59	0.59	—	—
PU2P9	1.9993	0.43	0.63	0.73	0.80	1.02	1.07	1.12	1.19	1.20	
PU3P9	1.9990	0.33	0.47	0.56	0.62	0.79	0.89	0.93	0.98	1.02	1.05
PU4P9	2.0012	0.59	0.75	0.92	1.01	1.25	1.29	1.29	—	—	—
PU5P9	2.0003	0.58	0.73	0.89	1.01	1.26	1.29	1.29	—	—	—
PU6P9	2.0017	0.67	0.84	0.98	1.08	1.33	1.40	1.42	1.42	—	—
PU7P9	2.0011	0.63	0.81	0.93	1.01	1.21	1.28	1.32	1.33	—	—

polyurethane layer was applied to the ceramic surface without adhesives; the high surface roughness was used as the only feature.

It has been determined that priming the ceramic material with resin improves the quality of coating. Increasing the polyurethane gelation time is also advantageous because it creates conditions for better de-gassing of the ceramic material. This results in a more homogenous surface that secures the proper tightness of the construction [2-6 and 17-21]. It has been determined that the technology of pouring a reactive polyurethane system is useful for producing the elastic polyurethane coating on metal as well as ceramic (concrete) surfaces.

The moisture content of a ceramic mass influences the quality of polymeric coating. Application of the coating in a dual-layer form is optimal because it improves the quality of the polymer's surface. This is due to the reduction in pore number on the ceramic surface and the increased strength of the elastic polyurethane coating.

RECYCLING

All polyurethanes obtained from glycolysates had similar tensile characteristics ranging from 13 to 15.5 MPa (Tab. 3). The polyurethane coded PU2 had lower elongation at break and sligthly smaller permanent elongation as compared to polyurethane PU1, which can be attributed to the higher content of cross-linking via allophanic and biuret bonds. The results of the TG analysis are presented in Fig. 6. Polyurethane displayed the temperature of the maximum mass loss T_{max} similar to that of glycolysates T_{max2}. The mass loss at this specific temperature most likely resulted from the degradation of the chains forming flexible segments. In Fig. 7 the FTIR spectra of the gaseous decomposition products of polyurethane at different temperatures, are shown. In the case of elastomer the carbonyl band has couple peaks at ca. 1730, 1745 i 1755cm^{-1}, which indicates high complexity of the mix of compounds. Similarly to glycolysates, the intense band at 1107cm^{-1} corresponding to the $\upsilon_{C\text{-}O\text{-}C}$ vibration indicates the presence of decomposition products of flexible polyether segments [20, 21].

***Tab. 3.** Tensile strength and relative elongation of polyurethanes obtained from glycolysates*

Sample	Extender	P_{NCO} [%]	Tensile strength [MPa]	Elongation at break [%]	Permanent elongation [%]
PU1	BDO	9.2	14.9	122.9	16.0
PU2	BDO	10.7	13.4	59.3	15.7
PU3	EG	10.0	15.6	61.3	14.9
PU4	BDO	10.0	14.9	62.2	15.4
PU5	HDO	10.0	14.8	71.6	17.6

The bands at 1612cm^{-1} and 1513cm^{-1} most likely correspond to a valent vibration of the $\upsilon_{C=C}$ aromatic ring. The characterization of the band marked in Fig. 7 has been presented in Tab. 4.

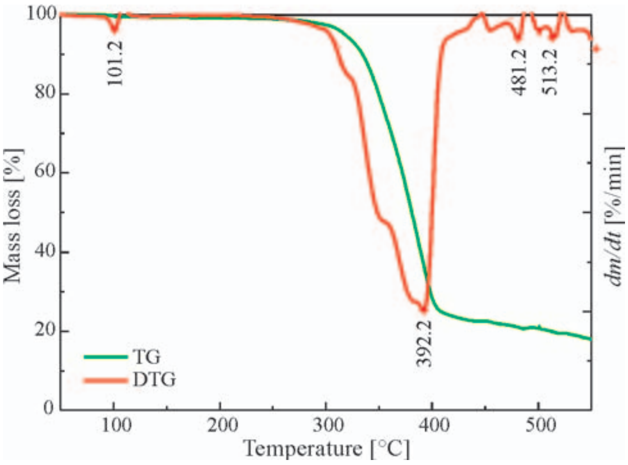

***Fig. 6.** TG and DTG curves obtained for PU1*

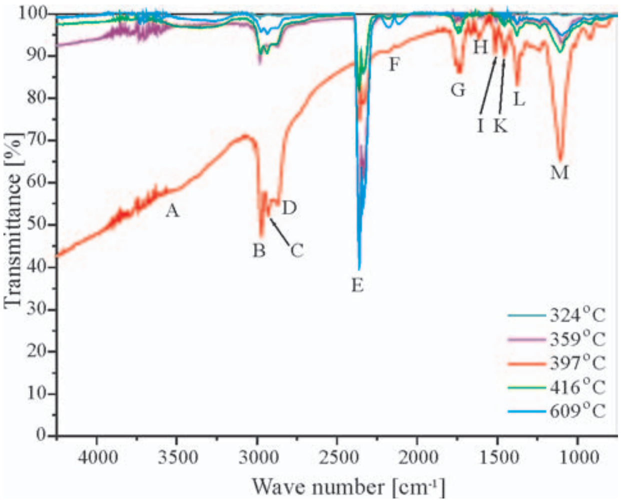

***Fig. 7.** FTIR spectra of gaseous decomposition products of polyurethane obtained from glycolysate*

***Tab. 4.** Description of the main absorption bands of gaseous decomposition products of polyurethane*

Symbol	Wave-number υ [cm^{-1}]	Vibration type or compound
A	3590	υ_{OH}
B	2970	$\upsilon_{CH3,as}$
C	2923	$\upsilon_{CH2,as}$
D	2871	$\upsilon_{CH3,sym}$
E	2360	CO_2
	2320	
F	2183	CO
	2117	
G	1745	$\upsilon_{C=O}$
H	1612	$\upsilon_{C=C}$
I	1513	
K	1452	$\delta_{CH3,as}$
L	1375	$\delta_{CH3,sym}$
M	1107	$\upsilon_{C—O—C}$

SUMMARY

The composition and methods for obtaining a prepolymer as well as its further processing by the RIM technique by using small molecule glycol extender, were elaborated. The used technique allows the production of durable polyurethane coating by applying the technology that does not require pre-heating of the steel elements and additional heating of polyurethane dispensed onto different surfaces. The conditions for obtaining coatings of the hybrid polyurethane-steel-ceramic type were defined. The recycling procedure was proposed for the waste polyurethane coating that comes from ship breaking or future pre-planned repair operations on the vessels. It will allow to obtain recycled semi-products, the so-called urethane oligomers, that have the properties and structures suitable for using them to manufacture new polyurethane products.

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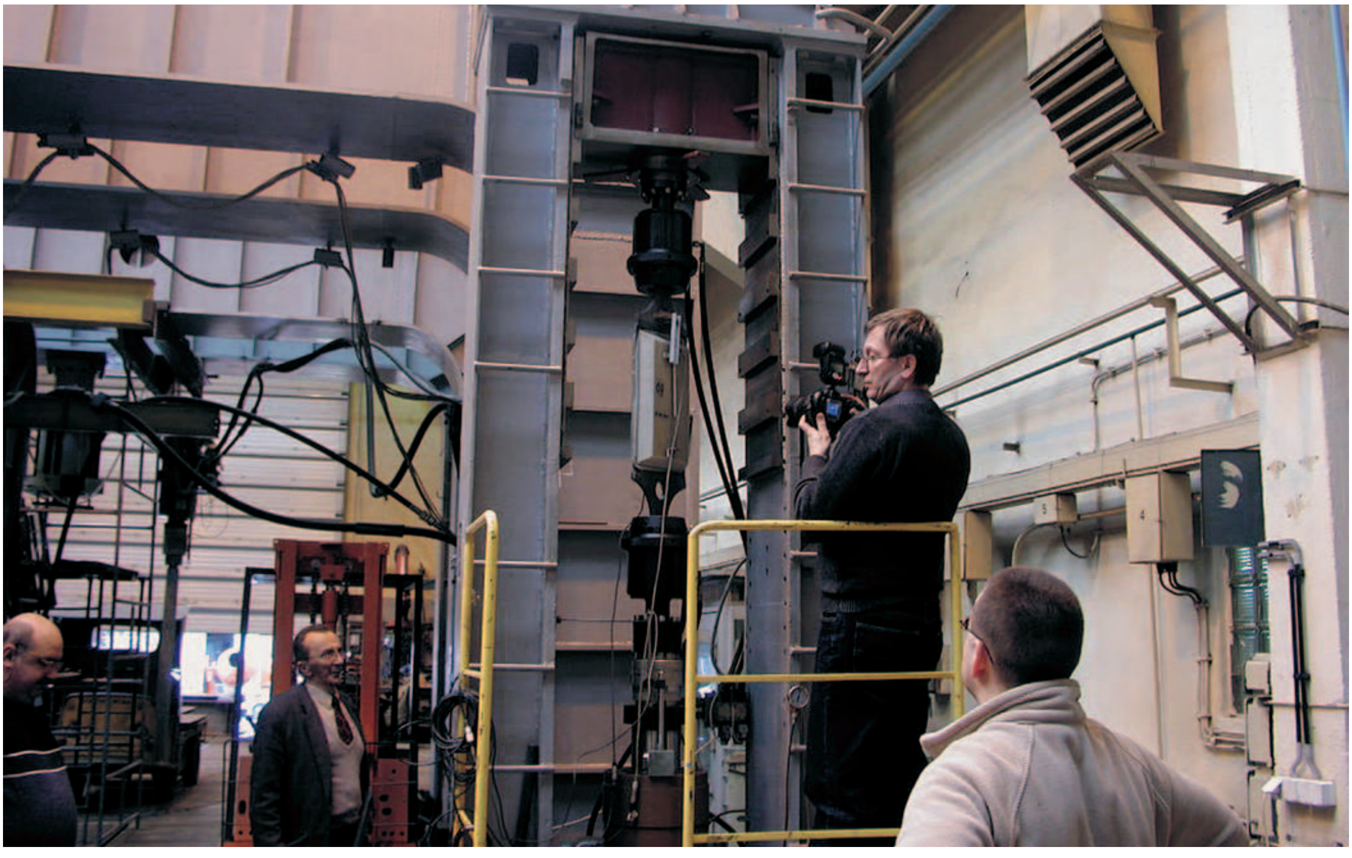

POLISH MARITIME RESEARCH Special Issue 2008; pp. 14-17
DOI: 10.2478/v10012-007-0071-4

Lightweight ceramsite concrete used as an additional protection of fuel oil tanks on ships

Marcin Jeżewski
Cezary Krasowski
Barg M.B. Gdańsk, Sp. z o.o.

ABSTRACT

Introduction of the semi-elastic barrier into ship fuel tanks requires of use of core material which will play role of carrier for elastic, fuel resistant layer. Such core material should be ligth, non reactive with water and fuel, fire resistant, corrosion neutral and finally easy applicable and relatively cheap. In paper the different problems like components, preparation, application as well as surface treatment for using of the light concrete as core material are presented.

Keywords: light concrete, core material, fuel tank protection

INTRODUCTION

Concrete is one of the most commonly applied materials for building structures. It has achieved its popularity due to specific properties which allow for its very wide application. The concrete applied directly *in situ*, the so called 'fresh concrete' is characterized by a high plasticity and workability, that makes it possible to form building structures almost without any limits. The concrete formed in the structure hardens very fast due to its hydratation processes, that gives appropriate strength and durability to building objects. A relatively simple way of concrete manufacturing, accessibility of its components, as well as wide range of its applications conditioned by many kinds of the material, have resulted in that the concrete is the most frequently used material for building structures. Such situation entails fast development of concrete technology. Many reserach projects aimed at improvement and modification of basic features of concrete are carried out worldwide. This is a material which continuously undergoes evolution, trying to cope with more and more sophisticated architectural requirements.

Concrete is a composite which is mainly formed of three components: binder, aggregate and water. Chemical admixtures and mineral additives, cut steel wires, natural and artificial fibres are also applied to it. After mixing the components together, a concrete mixture is obtained in the form of a viscous – plastic – solid body which is transformed into a solid body changing its features during further hardening (curing) process. The components of concrete of many types and classes can be found, that makes it possible to get mixtures of very different features and applications. The features can be additionally modified by introducing chemical admixtures and mineral additives. The so produced concrete is capable of transferring very large structural loads (high strength concretes), providing high durability for engineering objects (high durability concretes) or filling structural spaces (lightweight concretes), as well as it is suitable for many other applications in contemporary building industry.

The diversity of concrete mixtures, achieved by appropriate selection of particular types of main components, admixtures and additives, makes that their utility features begin drawing attention of other branches too, not only of building industry. One of the attempts to using the concrete features to other applications is the project of an additional protection layer made of concrete for ship fuel oil tanks and cargo tanks on tankers. This is a layer intended for separating ship's structure from a polyurethane coating which constitutes also a protective element of tanks. In the project the use is made of a relatively high strength of concrete associated with its rather low volumetric density (important for overall weight of ship), as well as its full fire resistance and durability implying a long service life. This paper presents an approach to implementation of concrete engineering and materials science to designing a concrete mixture which complies with criteria of the project. Below, ways of selection of particular components of the concrete, its manufacturing and material application, are presented.

SELECTION OF LIGHTWEIGHT CONCRETE COMPONENTS

One of the main features of concrete mixture deciding on selection of its components was its volumetric density. With a view of minimization of additional weight of ship one tried to obtain a concrete of as low volumetric density as possible with maintained maximum values of its strength and durability parameters.

A lightweight aggregate concrete distinguished – out of other kinds of concrete - by a relatively low volumetric

density at maintained high strength and durability parameters, best corresponds with the criterial parameters. Low value of the volumetric density is one of the basic features of lightweight concretes whose mechanical and physical properties depend on it. According to its definition the lightweight concrete volumetric density has not to exceed the value of 2000 kg/m^3.
It depends on:

- ★ kind and amount of aggregate
- ★ structure of concrete
- ★ amount of cement
- ★ amount of water absorbed by the aggregate.

Depending on a degree of concrete humidity the concrete volumetric density is differentiated into : that in dry state (of 0 - 3% humidity), that in dry-air state (of 6 - 9% humidity) and that in fresh state –after consolidation in curing phase (of 14 - 18% humidity). In common concretes volumetric density changes are small, but in the case of lightweight ones the changes can reach 20 - 25%.

The aggregate takes up a prevailing part of the whole volume of concrete (60-75%). Its appropriate selection is the most important element of designing the low-density concrete mixture. The best choice in this respect is associated with lightweight aggregates, and such kind of aggregate was selected in the case of the project in question.

Below (Fig. 1), values of the concrete volumetric density are presented depending on the used aggregate.

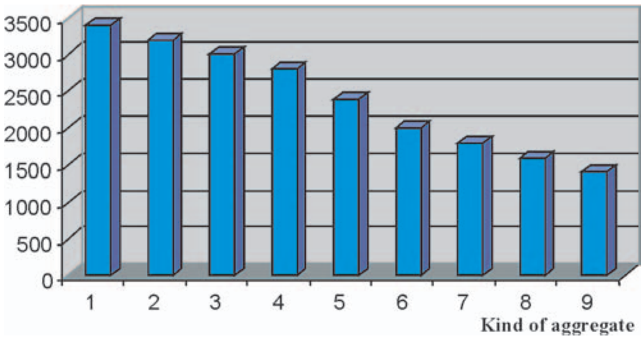

Fig. 1. *Concrete volumetric density in function of used aggregate kg/m^3.*
1-3 *– Heavy aggregates – e.g. granite, basalt,* ***4-6*** *– Usual aggregates – e.g. glacial gravels,* ***7-9*** *– Lightweight aggregates – e.g. pollytag, ceramsite*

Out of the large group of lightweight aggregates the ceramsite aggregate was selected. The ceramsite is obtained by burning silts and clays capable of bloating under exposure to heat. To this end the raw material is mixed with water till a dense consistence is achieved, and the so obtained mass is burnt in rotary furnaces in the temperature of abt. 1250°C. The bloating of clays and their possible refining leads to manufacturing a ceramsite of high strength and low density.

The ceramsite aggregate makes it possible to obtain the concrete of the strength reaching about 20 MPa and the volumetric density close to 1000 kg/m^3. Also, *llytag* ash-porite aggregate of a greater strength was considered. The strength increase was obtained at the expense of a significant increase of the volumetric density of the aggregate and for this reason it was rejected.

The next element of the designing of the mixture was to select an appropriate binding material. For lightweight aggregate concretes CEM I 32.5 Potland cements are used. Such material contains at least 95% of clinker and a minimum amount of additives. The so high content of clinker entails a very fast rise of concrete strength - even up to 90% of final strength - during the first week of curing. Maximum strength values of such cements have to be not lower than 32.5 MPa. The fast rise of concrete strength is of a great importance in practice as it makes it possible, after a short time from its application, to dismount constructional forms and to carry out further operations. This way down-time intervals due to concrete curing (hardening) can be minimized. To obvious drawbacks of application of CEM I cements belongs its large heat of hydratation, that leads to generation of thermal stresses and consequently can result in producing the cracks and weakening the structure. Such effects can be counteracted by adding fly-ash and applying a proper thermal insulation to a given element, that prevents from occurrence of large temperature gradients in it. The problem is mainly associated with large massive concrete objects.

Below (Fig. 2), the diagram of the mean strength rise of CEM I 32.5 cement slurry in function of time is presented.

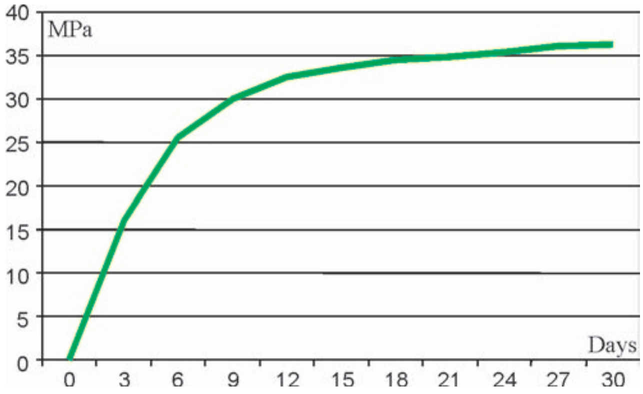

Fig. 2. *Strength rise of CEM I 32.5 cement slurry versus time*

For the designed lightweight aggregate concrete an addition of fly-ash was used. The fly-ash has a form of fine mineral dust of light-to-dark grey or light brown colour. It is mainly consisted of silicon, aluminium and ferric oxides. Moreover it contains, like natural rocks, various trace elements and shows a small amount of coke. As a result of thermal processing in fire chamber the fly-ash produced of hard coal enters the pozzolan reactions in presence of Ca in room temperature. This way, like in Portland cement hydratation process, tiny cristalic Ca-Si and Ca-Al hydrates which consolidate themselves into a hard rock material, are produced. The application of the additive in question was aimed at improvement of reologic parameters of concrete, that makes it possible to obtain an optimum workability of concrete mixture for applying it to ship steel elements.

The use of fly-ash makes also it possible to reduce consumption of cement – the most expensive component of concrete mixture – hence this is of a great economic importance. The fly-ash - due to its pozzolan features – takes part in mixture hardening. Also, as a result of it application, heat of hydratation is lowered and initial rise of concrete strength is mitigated. A plastifying admixture was a successive component used in designing the lightweight concrete. Admixtures are used for successive improvement of features of concrete mixture and hardening concrete. A wide range of action of the admixtures makes it possible to select an appropriate substance for almost any concrete mixture to be prepared.

The admixtures are usually added to concrete in an amount not greater than 5 % of cement mass. They can be both organic and non-organic substances of chemical, physical or chemical and physical influence. They can interact already during mixing the components or just in cured concrete. They can modify a few features, a part of which can become improved and the other – worsened.

In the case in question the *super-plastificator* admixture based on multi-carboxilate was applied. As a result of the application of the admixture, liquidity of the mixture - hence also its workability - was increased, and amount of applied water was lowered at maintained cement content, that led to a greater concrete strength. Such kind of admixture is intended for cements of fast rising strength.

For manufacturing the concrete mixture, tap water satisfying all relevant requirements according to PN-EN-standards was used.

MANUFACTURING THE LIGHTWEIGHT CERAMSITE CONCRETE

General recommendations

In accordance with a working recipe determined in advance, particular components of concrete are dosed in the following order : aggregate, possible fly-ash or natural sand additive, 1/2-3/4 amount of working water, cement and the remaining part of water. If aerating – plastifying additives are used their solution should be dosed last – after initial mixing the components. Before dosing the ceramsite its moisturing is recommended (using abt. 1/2 amount of working water). In the case of cement its dosing should be done by weighing, and in the case of aggregates – by weighing or volume measuring after determination value of bulk density of a given aggregate. Attention should be paid to water dosing. Changeable initial wetness of aggregate and progressing process of its moisturing can make it difficult to obtain a proper consistence of the mixture, which may require to be corrected.

The mixing should be performed mechanically – the best way is to apply forced, concurrent or backward mixing. Time of mixing should be not shorter than 3 min. If chemical aerating and plastifying additives are used the mixing time should be longer.

The ceramsite aggregate concrete mixtures which have less dense consistence, can be susceptible to segregating the components. Hence their transport should be performed in such way as not to cause segregation and changes in their composition. A seperate problem is the mixture's transport by pumping. High absorption capacity of aggregate makes that a part of working water - under pressure - developed during concrete pumping – is pressed into aggregate volume, that results in densification of the pumped mixture and consequently - blocking the pipelines. To make ceramsite concrete easy for pumping the aggregate should be mositured in advance and the concrete of a good workability should be designed.

Application of the ceramsite concrete mixture should be made uniformly over the whole surface of the form, and the throwing of the mixture from a greater height and placing of the concrete in the form of cone should be avoided as it may lead to partial segregation of the mixture. Application of aerating admixtures prevents the concrete mixture from segregation. Complete filling the form by the mixture should be finished before 30 min passing from the end of the mixing of components. Densification of the mixture should be done by using immersing vibrators of high frequencies and low amplitudes of vibration.

Recipe

The below given content of 1 m^3 of the concrete mixture was determined as a result of application of the general principles of concrete mixture designing with taking into account specificity of application of lightweight aggregates as well as results of verification of preliminary design assumptions by laboratory tests :

CEM I 32.5 cement – 350 kg
Ceramsite – 450 kg, fractions from 0-20 mm
Fly-ash – 150 kg
Water – 250 l
Super-plastificator – 0.3 % of cement mass.

The above given recipe was prepared for ceramsite concrete of a firm structure. Degree of filling the void spaces between aggregate particles by cement slurry should be not smaller than 85 %. The concrete of firm structure – in contrast to that having cavities or semi-firm one – is characterized by a greater compressive strength and greater workability, obtainable especially after adding fly-ashes and plastifying additives. Elaboration of a precise recipe for lightweight aggregate concrete mixture brings about certain difficulties. Because of high absorbability of lightweight aggregate as well as its suceptibility to segregation such recipe should be currently verified during production process and introduction of necessary corrections, mainly to amount of dosed water, should be possible.

Manufacturing process

In the case in question the first step in manufacturing of concrete mixture was to soak the aggregate in about 50% amount of working water. Next, in line with the above mentioned principles of sequencing the component addition, the components were mixed in a mixer up to the state of a uniform, non-separating, dense plastic mass. The remaining amount of working water was then added under continuous control of the slurry's consistence in order to prevent the mixture from excessive liquefaction, that could make correct application of the concrete impossible and its segregation easier. After obtaining its appropriate consistence and sufficient degree of mixing its components, the mixture was placed onto a ship plating element. For the mixture placing the immersing vibrators were applied in order to obtain its uniform distribution. Correctly manufactured concrete well spreads, does not leave void spaces and does not segregate or stratify its components.

Fig. 3. *Application of the concrete into the ship bottom structure*

The so prepared concrete mixture showed – during laboratory tests – the values of volumetric density in the range of 1100 – 1200 kg/m^3, and the values of the compressive strength after 28 days of curing - in the range of 12-14 MPa. Application of the pozzolan fly-ash additive makes it possible to expect a further rise of the compressive strength by about 10-15% of its value after 28-day curing.

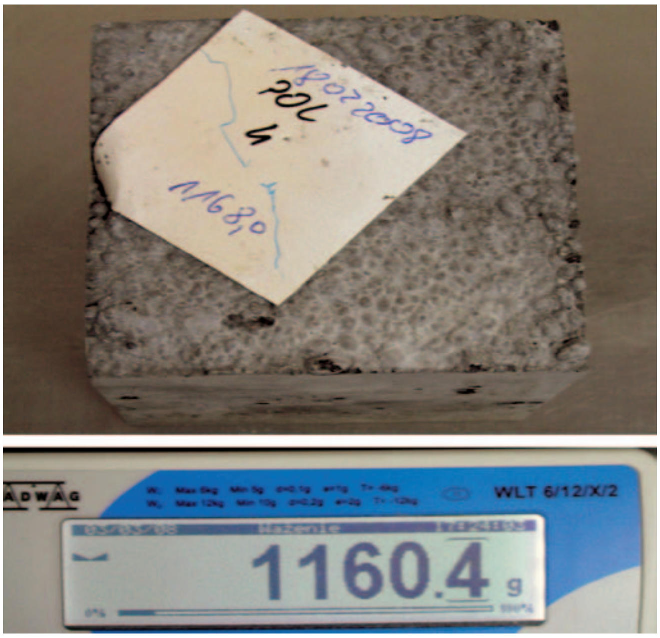

Fig. 4. *Exemplary view and weight of the ligth concrete specimen*

ADHESION BETWEEN CONCRETE AND STEEL

In the project in question the concrete used as a filler of void spaces in ship side structure, comes into direct contact with hull structural steel and polyurethane coating layer. Degree of concrete adhesion to those layers highly affects strength of the whole system. To improve adhesion of all the layers epoxy resins of two kinds with addition of quartz sand, which formed - together with the remaining components - the below presented structure, were applied :

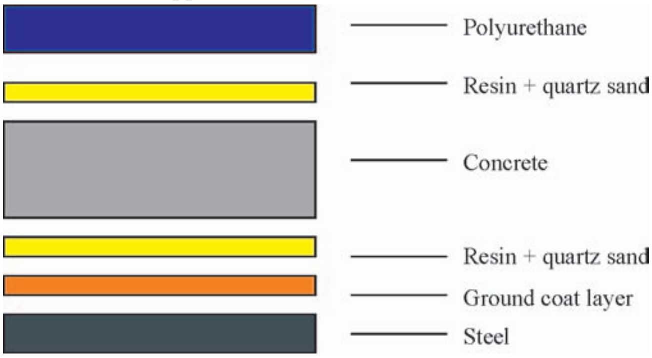

Fig. 5. *Layer structure of the typical elastic barrier supported by light concrete core*

Hull steel elements were covered with a ground coat layer of an epoxy resin of anti-corrosion properties. The layer is intended for protection of hull plating as well as for making it possible to apply successive layer of another kind. The next layer of epoxy resin of somewhat different properties, applied onto the ground coat, comes into direct contact with concrete. To increase contact area and adhesion power, the quartz sand poured directly on freshly laid resin, was used. On the so prepared background the concrete mixture was laid after about 48 h of curing. After the initial curing phase of the concrete its upper layer was also covered by the resin and quartz sand, that was aimed at improving the adhesion between the polyurethane layer and concrete.

In order to verify adhesion power between the polyurethane layer and concrete the pull-off test showing the degree of adhesion depending on materials applied to contact of layers, was performed.

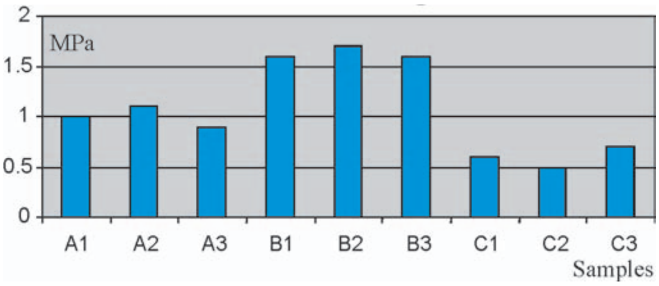

Fig. 6. *Pull-off strength test result of adhesion between concrete and polyurethane layer.* ***A*** *– samples with epoxy resin,* ***B*** *– samples with epoxy resin + quartz sand,* ***C*** *– samples without epoxy resin*

The test results clearly showed that the greatest degree of adhesion between polyurethane layer and concrete was obtained by applying the epoxy resin and quartz sand simultaneously.

During the pull-off testing much greater values of degree of steel-to-concrete adhesion were achieved for the samples with applied two layers of epoxy resin combined with quartz sand.

SUMMARY

- The lightweight aggregate concrete designed with application of the above presented principles is a very good filling material for protection barrier to be applied to ship fuel oil tanks and oil cargo tanks in tankers. Its volumetric density in the range of 1100-1200 kg/dm^3 and compressive strength ranging from 12 to14 MPa seem to be a good compromise between low unit mass and suficient strength. Correctly manufactured concrete mixture ensures also to obtain high durability, hence a long service life.
- In designing and manufacturing the lightweight aggregate concrete one should remember about specific features of such kind of concrete, especially about high absorbability of the aggregate which should be soaked in advance to avoid possible changes in mixture's consistence during its working process, consequently - changes in its properties assumed in the design stage.
- The application of epoxy resin layers greatly improves adhesion of particular layers of the protection system, that leads to rise of its strength and durability.
- The selection of all the specified components of lightweight concrete was performed not only with a view of technological reasons, but also economical ones.
- The selected components are widely available on the market at competitive prices.

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POLISH MARITIME RESEARCH Special Issue 2008; pp. 18-21
DOI: 10.2478/v10012-007-0072-3

Simulation of damage process of containership's side structure due to collision with a rock

Grzegorz Porembski
DesArt, Gdynia
Janusz Kozak
Gdansk University of Technology

ABSTRACT

This paper presents methods and results of a simplified numerical simulation of collision process of containership's side structure and a rock. Analysis of results of the modeling makes it possible to draw conclusions as to a character of the event as well as to estimate area and depth of damage caused by the penetrating rock, in order to select geometry of a filler and impermeable layer of 2nd protection barrier.

Keywords: collision, LSDYNA, FEM, numerical simulation.

INTRODUCTION

Models for analyzing ship collisions appeared in the 1950s to investgate consequences of collisions of ships for transport of radioactive materials. The models were later adjusted to other types of ships - barges, tankers or LPG/LNG carriers. A systematic review of approaches to collision modeling was published in 1997 [1], showing that several models based on different assumptions were in use. Generally, collision of ships is an event of large energy changes within a short time, usually described mathematically by the equations of energy conservation and moment equilibrium, and during which hulls of two ships come in mutual contact in such way that structural failure of at least one of them occurs.

MODELING THE COLLISION PROCESS

Collision between two ships is usually modeled as a non-elastic interaction. The interaction is defined as that in which a part of kinetic energy of colliding objects is transformed into other form of energy (e.g. work of damaging, heat etc) For the conditions of non-elastic collision the following equations of equilibrium of moments and energy can be defined [2,3,4]:

$$M_1V_1 + M_2V_2 = (M_1 + M_2)V_3 \qquad (1)$$

$$\frac{1}{2}(M_1V_1^2 + M_2V_2^2) = \frac{1}{2}(M_1 + M_2)V_3^2 + E_A + E_F \qquad (2)$$

where:
M_1 – mass tensor of hiting ship (together with added masses)
M_2 – mass tensor of hit ship (together with added masses)
V_1 – hiting ship velocity vector
V_2 – hit ship velocity vector
V_3 – velocity vector of both the ships after hit
E_A – amount of energy absorbed to deform and/or damage the structure
E_F – amount of energy transferred to surrounding water during collision.

As shown below, the perpendicular hit of bow of one ship against midship part of the other is an often occurring case of collision, Fig. 1 and 2.

Fig. 1. *Collision of m/t Gas Roman and m/v Springbok [2]*

During such hit – if the hiting ship is fitted with a bow bulb – a damage of hit ship's plating and supporting structure in its bilge zone below waterline, is possible. In this zone fuel oil tanks are usually installed. Hence such type of collision produces a risk of loss of tightness of a tank and leakage of fuel oil contained in it to surrounding water, that can result in environmental pollution. This paper presents a fragment of the work performed in the frame of the CORET project realized within the Eureka E! 3614 project. In the frame of the project, 3-D geometrical model of cargo part of a containership was elaborated. On this basis FEM model which initially served to perform several test analyses to verify modeling process regarding continuity and static effort, was built. After the verification the prepared model was used to make the below presented collision analysis.

Fig. 2. *A detail of side structure penetration during collision of m/t Gas Roman and m/v Springbok [2].*

NUMERICAL MODEL

The simulation was performed for the hull of 950 TEU containership of the following main particulars:

Overall length	138.10	m
B.p. length	132.00	m
Breadth	22.50	m
Depth to main deck	11.20	m
Design draught	7.60	m
Calculation draught	8.55	m

The entire cargo part of the ship was modeled. It was assumed that the hit against the rock occurs in the zone between the frame no. 86 and 121, therefore the FEM grid in the zone was made more dense, and in the remaining part of the model it was left relatively rough. In all the model, webs of the frames were modeled with finite shell elements, webs of the plating stiffeners in the zone between frame no. 86 and 121 – with finite shell elements, and in the remaining zones – with finite beam elements. And, flanges of the stiffeners and frames were modeled with finite beam elements within all the model, Fig. 3.

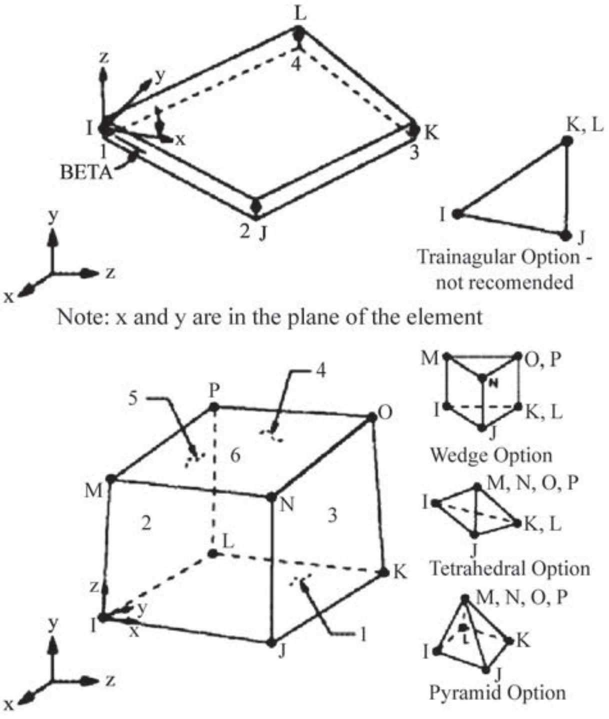

Fig. 3. *Forms of finite shell and solid elements appplied to the analysis*

To form the numerical model, 82574 shell elements and 1000 solid elements were used altogether, Fig.4.

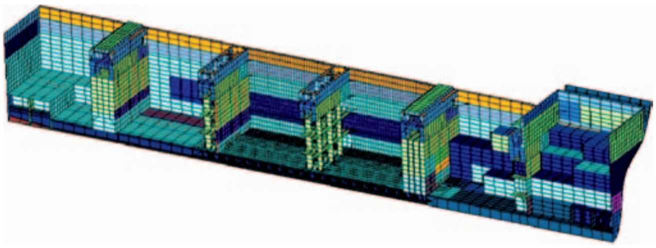

Fig. 4. *FEM model – a general view from the side of plane of symmetry (PS), the model with assigned attributes and FE grid*

Below, an enlargement of the model of the cargo hold part in the zone of planned hit against the rock, is presented in Fig. 5 - showing its view from the side of PS, and in. Fig. 6. – its view from the side of outer plating.

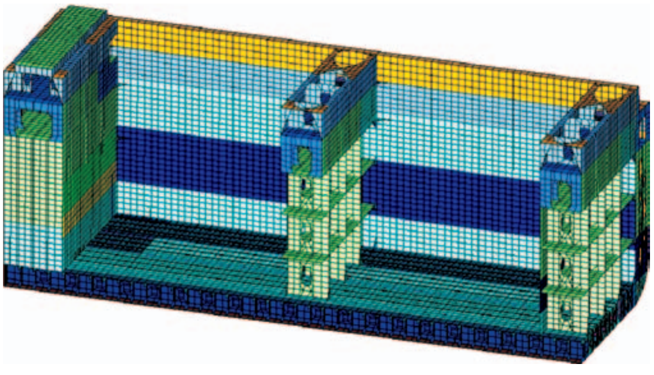

Fig. 5. *FEM model – the enlargement of its hold part in the zone of the planned collision, seen from the side of PS*

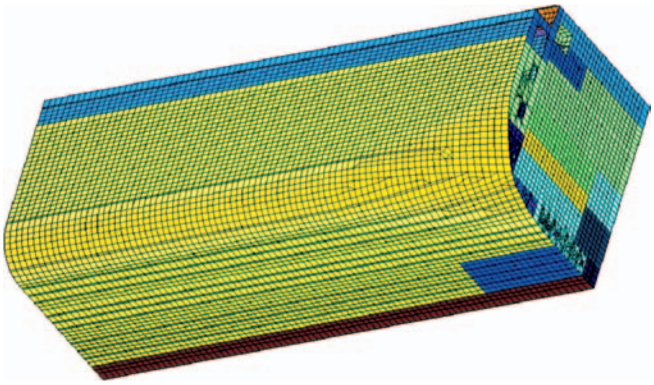

Fig. 6. *FEM model – the enlargement of its hold part in the zone of the planned collision, seen from the side of outer plating*

In the modeling process two kinds of material was used:

- for hull structures - steel of bilinear plasticity characteristics with determined damage limits, Tab.1.
- for the rock – a rigid and undeformable material.

Tab. 1. *Parameters of the selected steel used in calculations of the entire model of the cargo hold part of the containership*

No.	Description	Unit	Value
1	Young's modulus	GPa	200
2	Poisson's ratio	-	0.3
3	Density	kg/m^3	7865
4	Plasticity limit	MPa	310
5	Strain hardening modulus	MPa	768
6	Failure strain (deformation)	-	0.75

Relation between the rock and the ship's plating was assumed to be "the erosion contact", which means that to break continuity of the FE grid of the plating is possible.

The strain value equal to 0,75 was assumed to be the failure criterion.

SIMULATION OF COLLISION

The collision simulation was performed under assumption of a reverse process, i.e. such that the motionless ship hull was struck by the rock in horizontal motion with 20 mm/s speed, Fig. 7.

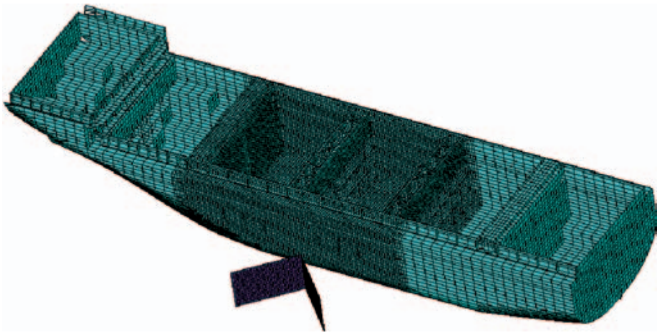

Fig. 7. *A view of the cargo part of the containership together with the colliding object*

During numerical calculations of ship-to-rock collision it is necessary to take into account the phenomenon of contact between different elements of the model. In the case in question it is difficult to predict which fragments will come into contact. The typical standard approach consisting in the use of a monitoring algorithm automatically determining which of the model elements take part in the contact, was assumed. The procedure for excluding the damaged elements made it possible to simulate the initial phase of the penetration of the ship plating structure by the rock and this way to cover the crucial phase of the collision.

Along with progressing penetration of the "rock" far into the plating structure its deformation occurs until the failure strain value is exceeded, that results in exclusion of the element. Below – in the successive figures –is presented the hull structure deformation process and associated rise of stresses up to occurrence of a hole in the side plating.

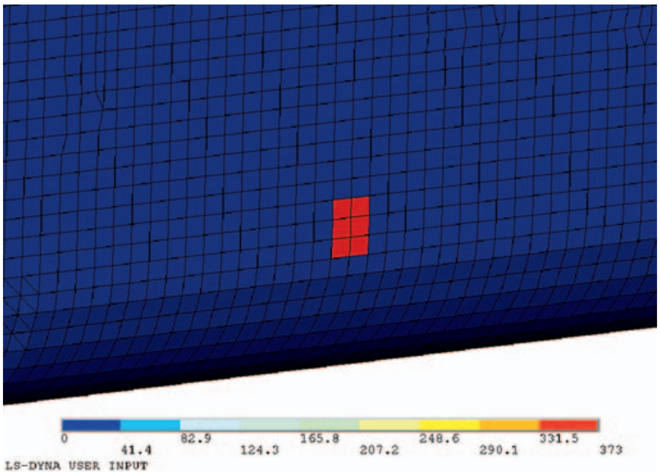

Fig. 8. *Reduced stresses in side plating just before its rupture*

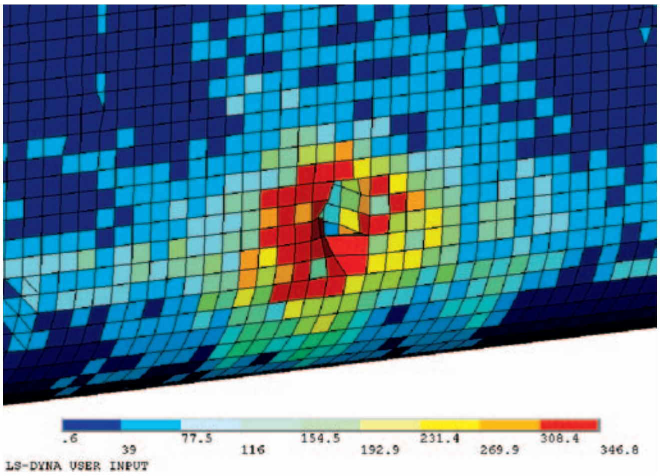

Fig. 9. *Reduced stresses at the instant of 51s passing from the beginning of collision – the moment of rupture of the outer plating*

An analysis of force distribution in elements of the colliding model made it possible to determine changes in reaction of ship-rock interaction in function of time. In the diagram of the changes (Fig.10) it can be observed that during the penetration process two points of maximum occurred. The first – after first 10 s of the collision, that corresponds with 200 mm depth of the penetration, the other – after 22 s of the collision, that corresponds with 440 mm depth of the penetration.

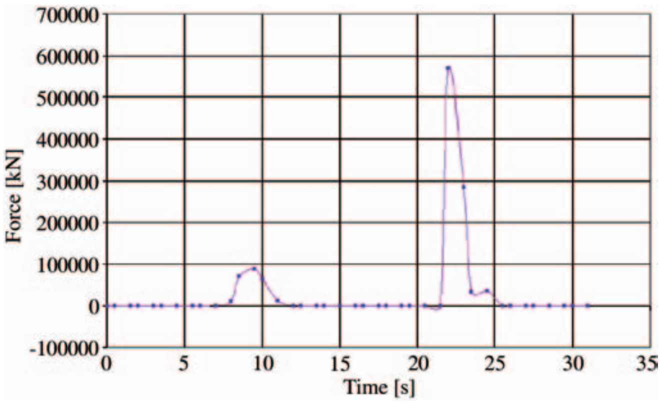

Fig. 10. *The force-time diagram of interaction between the side plating structure and the „rock"*

SUMMARY

- The performed simulation of the collision between the ship hull structure and rock is a slowly converging and time-consuming process because of introduction of necessary and deliberate simplifications. The obtained results illustrate structural damage resulting from penetration of the plating by the rock.

- The figures presenting the results show a stepped stress propagation and stepped damaging process of the side structure.

- Behaviour of the kind is influenced by the bilinear material characteristics as well as FE grid density. A greater grid density could mitigate the steps, however the character of the process will remain the same.

- The force-time diagram of interaction between the side structure and rock shows that the modeling metod applied to the simulation yields a character of local peaks up to the instant when the exclusion conditions of elements (failure strain >0,75) is reached.

- More realistic values could be obtained if failed elements were left during simulation.

- Application of the excluding procedure of the failed elements made it possible to simulate the initial phase of penetration of the plating structure by the rock, and this way to capture the crucial moment of the collision.

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POLISH MARITIME RESEARCH Special Issue 2008; pp. 22-26
DOI: 10.2478/v10012-007-0073-2

Numerical calculations of behaviour of ship double-bottom structure during grounding

Karol Niklas
Gdańsk University of Technology

ABSTRACT

The idea of the CORET project consists in adding, to the existing construction, special polymer-concrete coatings intended for the increasing of ship's capability against losing structural tightness during collision or grounding. In order to correctly design the protective barriers, to perform relevant numerical simulations is necessary. The elaborating of numerical models of ship structure behaviour during collision is very complicated and requires auxiliary simulations (on submodels) to be performed. This paper is devoted to elaborating a numerical model of a fragment of ship double-bottom structure. On the basis of experimental tests it was possible to verify and calibrate the numerical model which may be used in further design work aimed at the increasing of crashworthiness of structure during collision.

Keywords: numerical simulation, grounding, collision, CORET project, LS-DYNA software

INTRODUCTION

In the frame of the EUREKA E!3614 CORET project a proposal has been given on application, to ship double-bottom structure, additional polymer-concrete protective barriers. In the case of ship's grounding, when its double bottom outer plating is torn up, such additional barrier can ensure tightness to tanks filled with fuel oil. Numerical simulations of ship grounding are carried out to design ship side structure in such a way as to be it capable of absorbing as large amount of energy as possible (at maintained tightness). The elaborating of numerical models of ship structure behaviour during collision is very complicated and requires auxiliary simulations to be performed. The most difficult task is to model a fragment of double bottom structure in the vicinity of its contact with ground. In this zone the structure undergoes large deformations, buckling, plastic flow and tearing phenomena. For this reason a submodel of the collisione zone was produced to form a model of ship double bottom fragment, which would follow - in a possibly reliable way - real structure behaviour during collision. On the basis of experimental tests it is possible to verify and calibrate the numerical model for using it further in a larger ship structure model. The below presented simulation of indenting a sphere into a fragment of ship bottom structure, being the most difficult task, is thought to aid - after making a physical experiment to verify and calibrate it - the elaborating of the model of ship double bottom structure fragment during ship grounding. In the future the model may be also used to perform calculations for designing a ship double bottom structure of an increased capability against losing its tightness during ship grunding or collision.

FEM NUMERICAL MODEL

The indenting of the sphere into a ship structure fragment by means of a hydraulic ram was simulated with the use of a numerical model. The FEM model geometry and real structure model is presented in Fig. 1. The model's analysis was made by using the explicite solver of LS-DYNA (v9.71) software. The quasi-static simulation conditions were assumed with a view of relevant conditions for the model calibration experiment. To accelerate the calculations the sphere velocity equal to 0.8 m/s was assumed. The diameter of the sphere was equal to 0.3 m, and it was modeled as a solid body.

The boundary conditions adequate to fixing the model during the experimental tests, were assumed (Fig. 2). Though the small velocity value allows for neglecting the dynamic aspects, it makes time of the calculations much longer.

Duration time of the simulation, assumed equal to 5s, and the maximum time step possible to be applied, made it necessary to introduce mass scaling in order to shorten time of calculations. The model consisted of 18.000 shell elements. To lower the total number of elements by making the FE grid more dense in the regions of the greatest expected stresses, is rather not effective in the calculations which take into account large non-linearities. Apart from an unknown influence of the more dense grid on calculation results and necessity of its checking, the effect of lowering the total number of elements would be reduced by a shorter time step. As the time step is selected for the smallest element of the model hence the grid concentration would be rather not effective in the case in question.

Fig. 1. Numerical model and real structure model of a fragment of ship double bottom structure

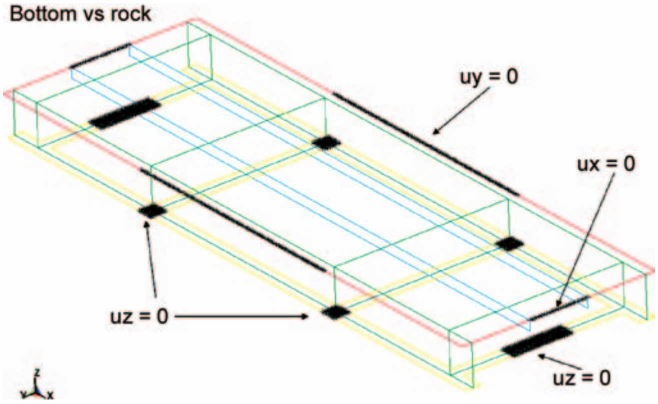

Fig. 2. Boundary conditions assumed for the numerical model

To apply greater elements to the whole model is also not possible because of the reasons given below. Very large deformations expected during the simulation (up to complete tear-up of the plating) allow for using only a certain number of FEs per span of structural element. In the structure in question the small-depth stiffener (flat bar) is that which determines the smallest dimension. For correct modeling the strictly elastic deformations one FE per span of the stiffener is sufficient. For correct taking into account the buckling and ultimate strength phenomena four FEs per stiffener span are necessary.

If the modeling of large plastic deformations is required, especially those around „plastic hinge", the minimum number of FEs will amount to 16.

The elaborated model satisfies all the above mentioned conditions resulting from numerical aspects.

The next aspect of building the numerical model is to select an appropriate FE.

The LS-DYNA software contains a rich data base of shell FEs. The usually assumed shell element is that of Belytschko-Tsay type (BT), based on ideally flat geometry, which is very effective during calculations. Until cracks and very large deformations are not involved the BTelement correctly represents the behaviour of thin-walled steel structures during collision [1, 2]. However the necessity of taking into account very large deformations and plate tearing-up, induces to select more sophisitcated FEs, namely: the Belytschko-Wong-Chiang FE and 16 FE (fully integrated shell). For the model, influence of FE selection on calculation results should be also analyzed. The successive aspect is to select a form of shell FE (triangular or quadrilateral), arrangement of FEs (uniformly arranged or not), as well as a number of integration points. As regards numerical errors a better solution is to select obviously a quadrilateral FE, however predefined lines of nodes constitute the main drawback of a regular grid composed of quadrilateral FEs, which often make real crak directions during plate tearing-up false [3]. Simultaneously, the using of triangular FEs, even to control numerical errors, is rather unfavourable. The influence of the grid on calculation results, especially in the case of highly non-linear calculations, may be very large [1]. It seems reasonable to investigate influence of using various grids in the most interesting zones of structure. The phenomenon of contact is a successive non-linearity taken into account in the model in question. In the analysis, automatic algorithms of contact to monitor distances of particular nodes during each time step, are applied. The static friction coefficient equal to 0.74 and dynamic one equal to 0.57 (steel-to-steel) was assumed.

The model of elastic-plastic material behaviour following the stress-strain relationship (based on tensile test) and having strain-dependent plasticity limit (acc. Cooper-Simonds model), was assumed. The material failure phenomenon was taken as the strain (elongation) criterion. When strain in any element exceeds its limit value the element is automatically excluded from the model and the calculations based on the eroded grid, are continued. The influence of critical strain (elongation) on calculation results was analyzed in the work [4]. The limit strain of FE is defined in function of FE's size. The critical strain value of the best fit can be determined by simulating the tensile test of a sample and calibrating the model with the use of real sample test results.

RESULTS

The energy equation shown in Fig. 3, is calculated for each time step. The energy is composed of elastic strain energy and work done for plastic deformation. And, the external work contains work done by applied forces, pressures, as well as that done by elements of the applied boundary conditions

$$\underbrace{E_{kin} + E_{int} + E_{si} + E_{rw} + E_{damp} + E_{hg}}_{\boxed{\textbf{Total Energy } E_{total}}} = E_{kin}^{0} + E_{int}^{0} + W_{ext}$$

where:

E_{kin} – kinetic energy
E_{int} – internal energy
E_{si} – sliding energy
E_{rw} – rigidwall energy
E_{damp} – damping energy
E_{hg} – hourglassing energy
E_{kin}^{0} – kinetic energy (t = 0)
E_{int}^{0} – internal energy (t = 0)
W_{ext} – external work

Fig. 3. Energy equation

(displacements, velocities and accelerations). In Fig. 4 the particular total energy components are presented. As it can be observed, internal energy is of the greatest share. The energy increases until the limit strain values assumed for plating elements are not exceeded, and after plate tearing-up it maintains almost constant value. Friction energy a little only contributes in the total energy and its influence grows after plate tear-up. Percentage share of the kinetic energy resulting from possible increase of the sphere's velocity in order to reduce time of calculations, would be negligible, hence quasi-static conditions have been maintained. The maximum value of the reaction force at supports along z- axis (Fig. 5) is equal to 1.15 MN.

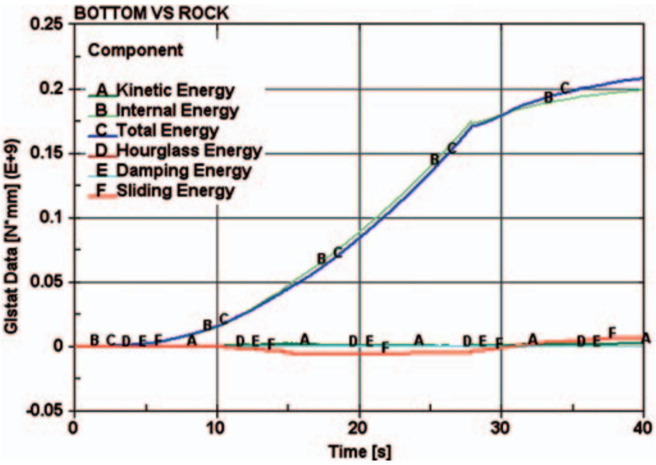

Fig. 4. *Total energy and its components*

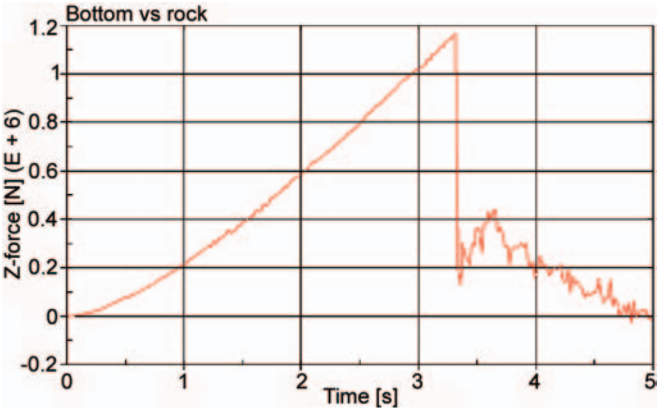

Fig. 5. *Total reaction force at supports along z - axis.*

Fig. 6 presents the reduced (Mises) stresses in successive time instants during simulation. The tear-up of plating takes place after 3.3s and covering the distance of 266 mm. Fig. 7 shows the stress image after stopping the simulation. In the instant *t* =3.3 s the deformations of particular elements of the model are as follows: large-depth stiffeners - 15.8 mm (Fig. 8); small-depth stiffeners - 129.4mm (Fig. 9); side plating - 262.9 mm (Fig. 10).

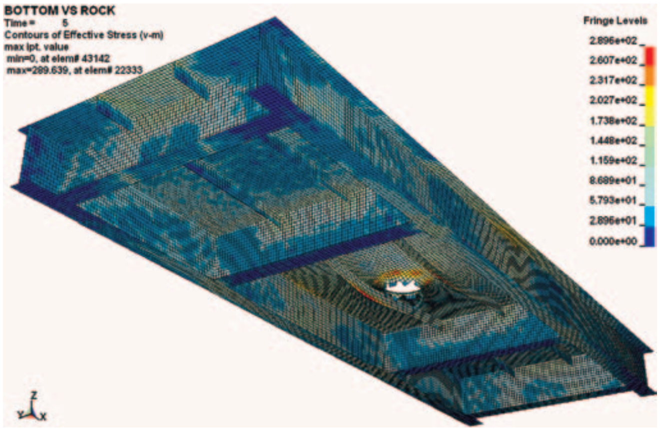

Fig. 7. *Image of reduced (Mises) stresses (t=5s)*

Structural failures caused by indenting the sphere into side plating are of a local character.

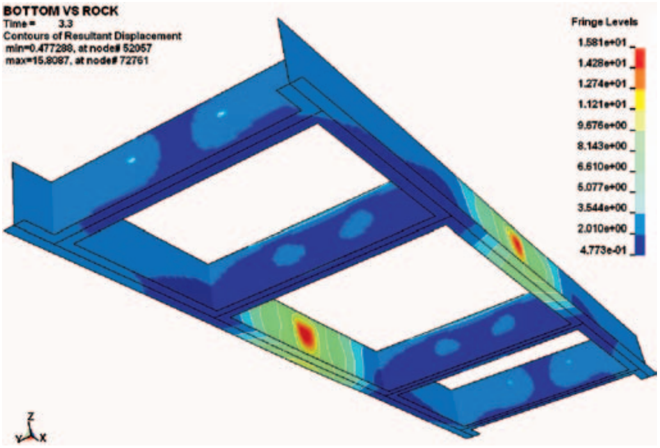

Fig. 8. *Deformations of large-depth stiffeners*

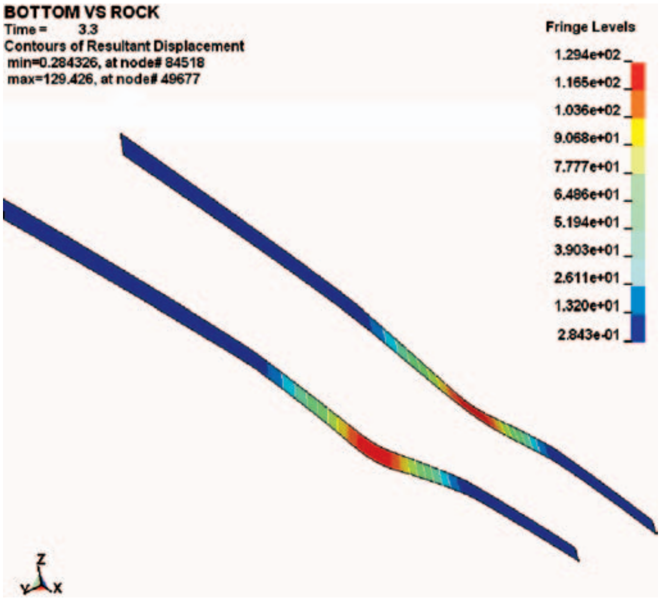

Fig. 9. *Deformations of small-depth stiffeners*

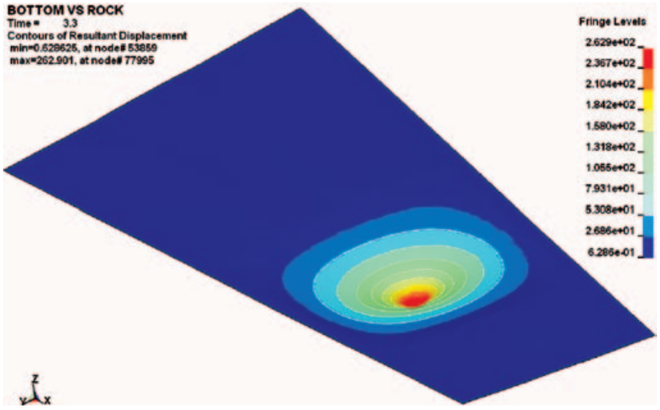

Fig. 10. *Deformations of side plating*

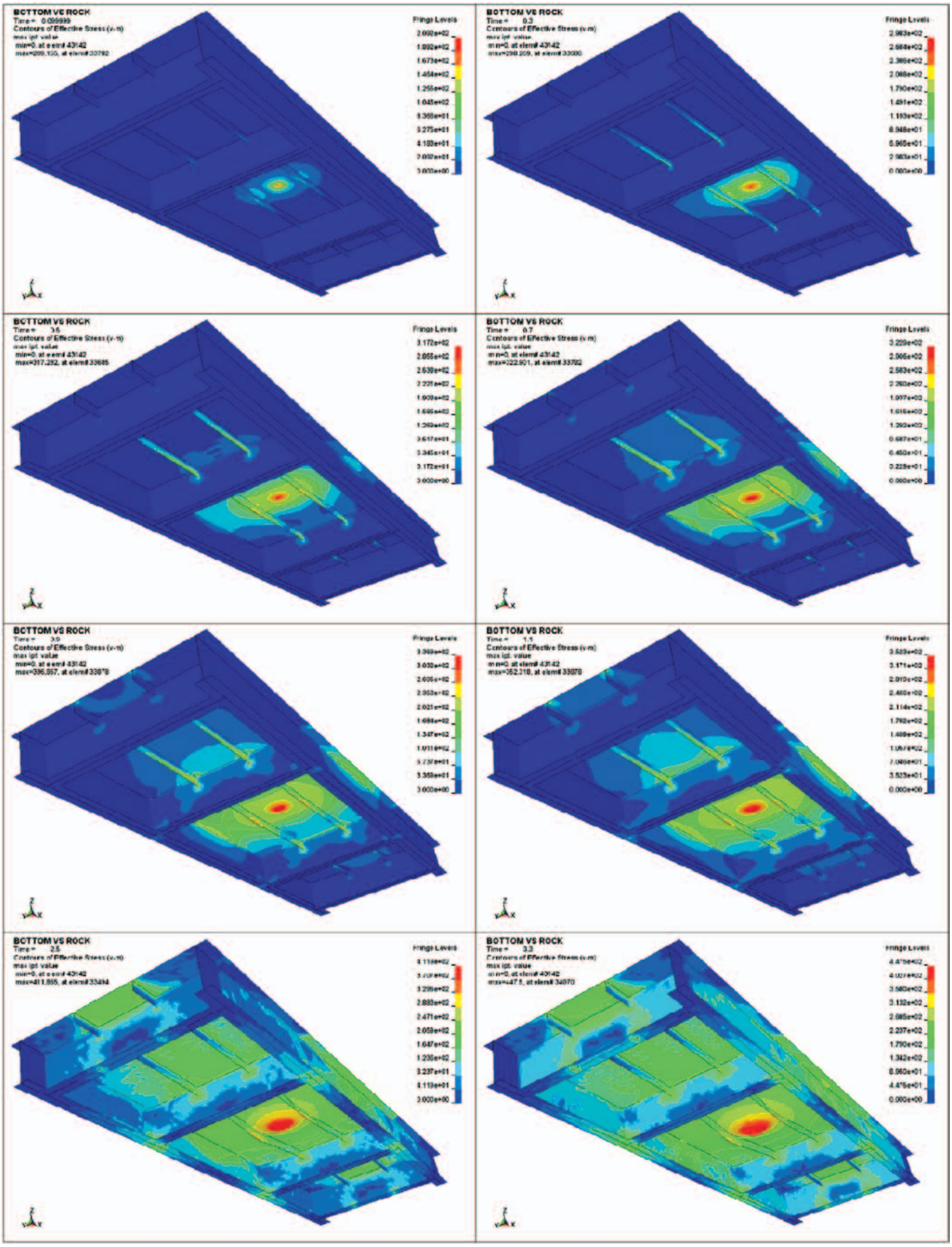

Fig. 6. *Reduced (Mises) stresses in successive time instants (down from top, row by row: t = 0.1, 0.3, 0.5, 0.7, 0.9, 1.1, 2.5, 3.3s)*

SUMMARY

Ship traffic statistics of the last years as well as predictions for the coming ten years leave no doubts that risk of ship collision and grounding is still a very serious problem.

Many research projects on safety improvement have been carried out by many scientific centres worldwide, e.g. [5-10]. Some problems have been solved so far. Most attention has been focused on the increasing of structural capability of tankers against losing tightness resulting from collision or grounding. Until 2015 all single-skin tankers have to be withdrawn from service. Simultaneously, size of new tankers of various types has so increased that the amount of fuel oil carried out onboard for their propulsion has become comparable to cargo capacity of a small tanker. Single-skin fuel oil tanks are often located in ship's double bottom. In the case of ship's grounding danger of ecological disaster resulting from outer plating tear-up is similar to that in the case of a single-skin tanker. Therefore the attempt at decreasing the risk of loss of tank tightness in the case of collision, by applying, to the typical ship structure, additional polymer-concrete coatings, has been undertaken. To this end, the numerical simulations of collision were used. However auxiliary simulations on submodels were necessary to make the numerical model fully adequate to real conditions. Such submodels usually cover structural fragments most difficult for modeling, and their verification and calibration is done in an experimental way. This work has been aimed at the elaboration of the double-bottom structure fitted with additional polymer-concrete layers, capable of preventing fuel oil leakage in the case of collision.

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POLISH MARITIME RESEARCH Special Issue 2008; pp. 27-30
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Calculation of oil outflow from fuel oil tanks of a containership with polymer coatings applied to double bottom tanks – in the light of Resolution MEPC.141(54) of IMO

Grzegorz Władziński
Zbigniew Rutkowski
Gdansk University of Technology

ABSTRACT

Introduction of the semi-elastic barrier into fuel tanks rise environmental protection level in case of ship collision or grounding. Last law regulations requires change of localisation of fuel tanks in ship structure in a such way to increasing distance between fuel and surounding water. Application of semielastic barrier into fuel tank make possible to localise fuel tanks in double bottomspace. Calculation of hipothetical outflow of fuel from damaged fuel tan in case of application of senielastic barier is presented.

Keywords: fuel tank protection, outflow calculation

INTRODUCTION

For the presented calculation analysis an existing design of SINE202 containership was used. The technical design of the containership having typical arrangement of deep fuel oil tanks, was elaborated entirely by the SINUS design office. All amount of fuel oil contained in the deep tanks was accommodated in double-bottom tanks due to application of polymer coatings in them. This way, the so designed modernization of the ship made its cargo capacity greater. For the new arrangement of fuel oil and ballast tanks a hypothetical fuel oil outflow was calculated for various values of hull damage probability.

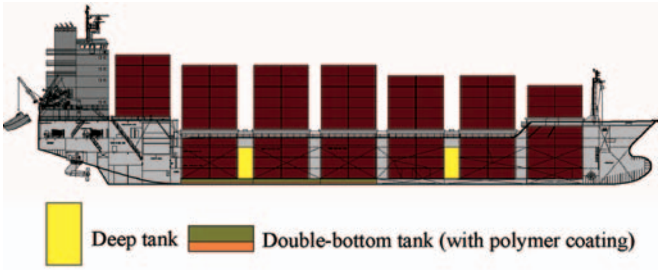

Fig. 1. SINE 202 ship – the analyzed object

Ship main dimensions:

Length overall	138.10 m
Length b.p.	132.00 m
Breadth	22.50 m
Depth	11.20 m
Design draught	7.60 m

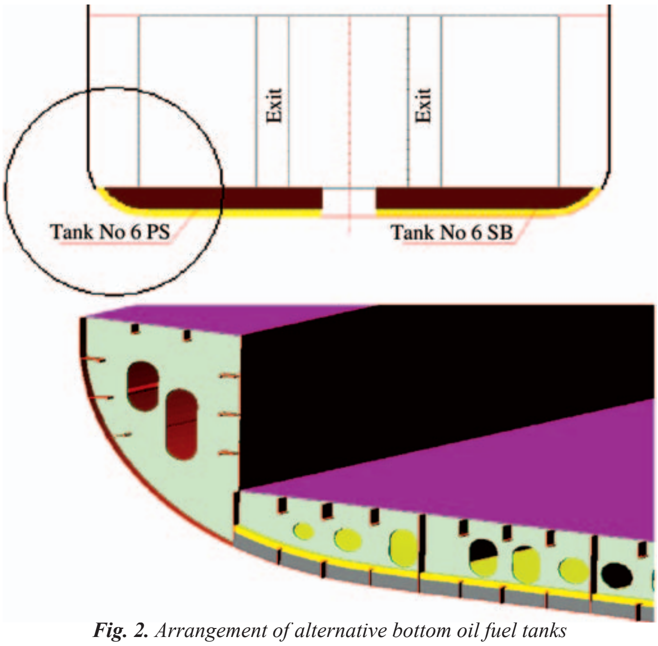

Fig. 2. Arrangement of alternative bottom oil fuel tanks on board the containership

The application of polymer coatings to tanks of the considerd ship was aimed at making it possible to transfer fuel oil from the deep tanks located between cargo holds to the low-depth double-bottom tanks, at simultaneous maintaining compliance with conditions imposed by rules. Such design action could result a.o. in possible using the resulting free space between holds for other purposes.

Though the theoretical distance between fuel oil and ship outer plating has been made radically smaller the level of ship protection against possible oil outflow (in the case of outer plating failure) has been maintained due to physical and chemical properties of the applied protective coatings.

REQUIREMENTS FOR MACHINERY COMPARTMENTS ONBOARD ALL SHIPS ACCORDING TO RESOLUTION MEPC.141(54) [1]

Regulation 12 - Tanks for oil residues (sludge)

1. Every ship of 400 GT or more shall be fitted with a tank or tanks of adequate capacity with a view of kind of its machinery equipment and time of voyage, to serve for storing oil residues (sludge) which cannot be treated in any other way in compliance with provisions of this Annex, and which are produced as a result of centrifugation of fuel and lubricating oils and oil leakages in machinery compartments.
2. Piping leading to and from such sludge tanks shall not have other direct outboard connections than the standard discharge connection defined in the Resolution's provision.
3. On ships delivered after 31 December 1979, the oil residue tanks shall be so designed and built as to made their cleaning and discharging the residues to receiving devices, easier.

Regulation 12A – Fuel oil tank protection

This regulation shall apply to all ships with an aggregate fuel oil capacity of 600 m^3 and above which are delivered on or after 1 August 2010.

For the purpose of this regulation, the following definitions shall apply:

Length	(L)
Waterline	(dB)
Breadth	(B)
Fuel oil	
Breadth	(B_B)
Fuel oil tank	
Depth	(D_S)
Light ship draught	(d_{LS})
Load line draught	(d_S)
Partial load line draught	(d_P)

☆ “Length (L)” means 96% of the total length (L’) on a waterline at 85% of the least moulded depth measured from the top of the keel, or the length from the foreside of the stem to the axis of the rudder stock on that waterline, if that be greater. In ships designed with a rake of keel the waterline on which this length is measured shall be parallel to the designed waterline. The length (L) shall be measured in metres.

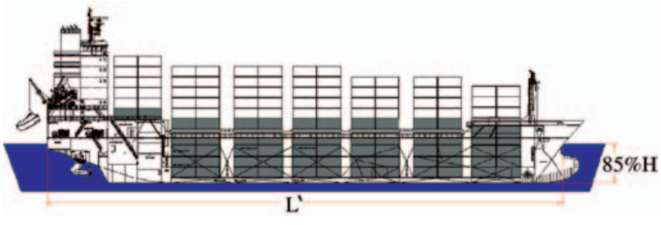

Fig. 3. Definition of the calculation length according to regulation 12A

☆ “Breadth (B)” means the maximum breadth of the ship, in metres, measured amidships to the moulded line of the frame in a ship with a metal shell and to the outer surface of the hull in a ship with a shell of any other material.

☆ “Breadth (BB)” is the greatest moulded breadth of the ship, in metres, at or below the waterline (dB).

☆ “Depth (DS)” is the moulded depth, in metres, measured at mid-length to the upper deck at side. For the purpose of the application, “upper deck” means the highest deck to which the watertight transverse bulkheads except aft peak bulkheads extend.

☆ “Fuel oil” means any oil used as fuel oil in connection with the propulsion and auxiliary machinery of the ship in which such oil is carried.

☆ “Fuel oil tank” means a tank in which fuel oil is carried, but excludes those tanks which would not contain fuel oil in normal operation, such as overflow tanks.

☆ “Fuel oil capacity” means the volume of a tank in m^3, at 98% filling.

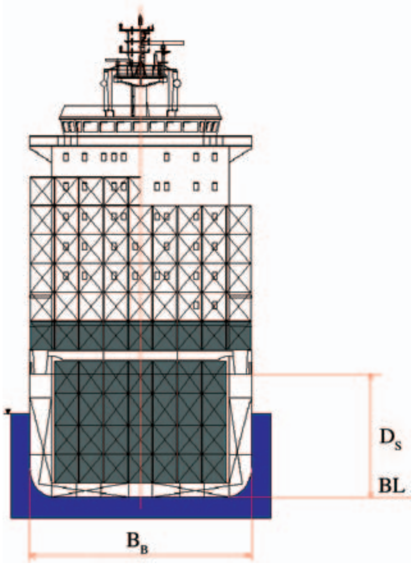

Fig. 4. Definition of the calculation depth and breadth according to regulation 12A

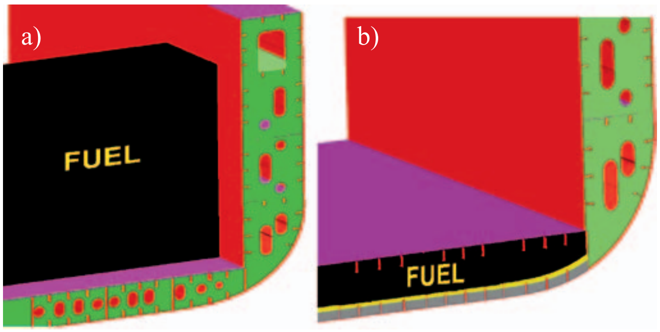

Fig. 5. a) Fuel oil in deep tank, b) Fuel oil in double bottom tank

☆ „Light ship draught (d_{LS})” is the design draught measured at mid-length (L/2), corresponding to light ship mass.

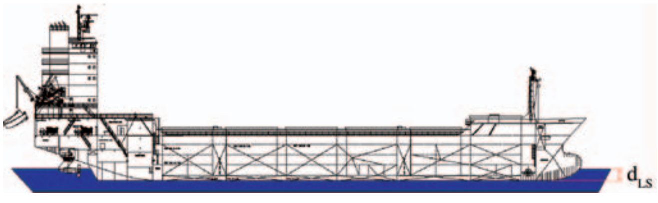

Fig. 6. Definition of the light ship draught according to regulation 12A

☆ “Load line draught (dS)” is the vertical distance, in metres, from the moulded baseline at mid-length to the waterline corresponding to the summer freeboard draught to be assigned to the ship.

Fig. 7. *Definition of the load line draught according to regulation 12A*

- "Partial load line draught (dP)" is the light ship draught plus 60% of the difference between the light ship draught and the load line draught dS. The partial load line draught (dp) shall be measured in metres.

  d_p: Partial load draught $= d_{LS} + (d_S - d_{LS})\cdot 60\%$ [m]

- "Waterline (dB)" is the vertical distance, in metres, from the moulded baseline at mid-length to the waterline corresponding to 30% of the depth DS.

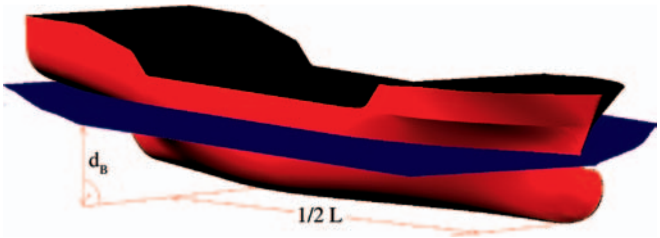

Fig. 8. *Definition of the base waterline according to regulation 12A*

Par. 6. For ships, other than self-elevating drilling units, having an aggregate fuel oil capacity of 600 m^3 and above, fuel oil tanks shall be located above the moulded line of the bottom shell plating nowhere less than the distance h as specified below:
h = B/20 m or,
h = 2.0 m, whichever is the lesser.
The minimum value of h = 0.76 m.

In the turn of the bilge area and at locations without a clearly defined turn of the bilge, the fuel oil tank boundary line shall run parallel to the line of the midship flat bottom as shown in Fig. 9.

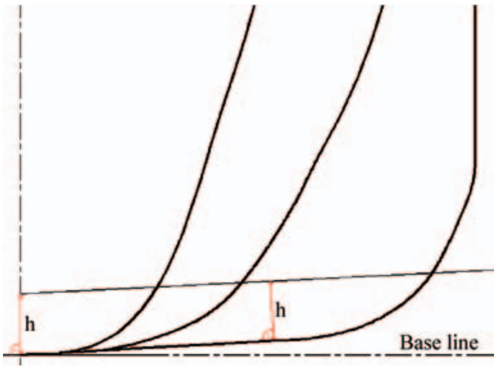

Fig. 9. *The oil fuel tank boundary line running parallel to the line of the midship flat bottom*

Par. 7. For ships having an aggregate fuel oil capacity of 600 m^3 or more but less than 5,000 m^3, fuel oil tanks shall be located inboard of the moulded line of the side shell plating, nowhere less than the distance w which, as shown in Fig. 10, is measured at any cross-section at right angles to the side shell, as specified below:
w = 0.4 + 2.4 C/20,000 m

The minimum value of w = 1.0 m, however for individual tanks with a fuel oil capacity of less than 500 m^3 the minimum value is 0.76 m."

Par. 8. For ships having an aggregate fuel oil capacity of 5,000 m^3 and over, fuel oil tanks shall be located inboard of the moulded line of the side shell plating, nowhere less than the distance w which, as shown in Fig. 10, is measured at any cross-section at right angles to the side shell, as specified below:
w = 0.5 + C/20,000 m or
w = 2.0 m, whichever is the lesser.
The minimum value of w = 1.0 m.

As applied to SINE202 ship:
To SINE 202 ship the following quantities apply:
h = B / 20 m or h = 2.0 m; whichever is the lesser.
The minimum value of w = 1.0 m

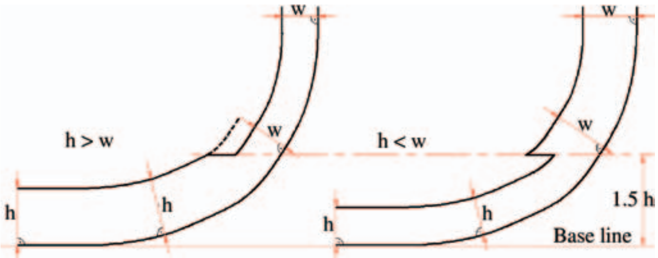

Fig. 10. *Fuel oil tank boundary lines for the purpose of par. 7 and 8*

Par. 11. Alternatively to par. 6 and either 7 or 8, ships shall comply with the accidental fuel oil outflow performance standard specified below:

The level of protection against oil fuel pollution in the event of collision or grounding shall be assessed on the basis of the mean oil outflow parameter, as follows:

$$OM < 0.0157\text{-}1.14E\text{-}6\cdot C \quad 600\ m^3 = C < 5{,}000\ m^3$$

where:
OM = mean oil outflow parameter
C = total fuel oil volume.

As applied to SINE202 ship:

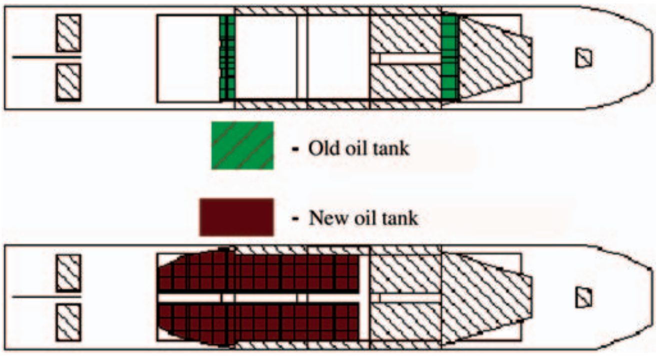

Fig. 11. *Arrangement of oil fuel tanks onboard the analyzed ship*

As for the ship in question the total volume of its fuel oil tanks - both before and after their modification - does not exceed 5000m^3 hence the above given formulae apply to it.

According to par. 11 the following general assumptions shall be used when calculating the mean oil outflow parameter:

- The ship shall be assumed loaded to the partial load line draught (d_P) without trim or heel;
- The nominal density of the fuel oil (ρ_n) shall generally be taken as 1,000 kg/m^3. If the density of the fuel oil is specifically restricted to a lesser value, the lesser value may

be applied; and the permeability of each fuel oil tank shall be taken as 0.99.

As applied to SINE202 ship:

For the relevant calculations of the ship in question the fuel oil density $\rho_n = 0.9\ \mathrm{t/m^3}$ and the permeability of fuel oil tanks equal to 0.99 was assumed (Fig. 12).

⇨ The mean oil outflow shall be calculated independently for side damage and for bottom damage and then combined into a non-dimensional oil outflow parameter OM, as follows:

$$OM = (0.4\ OMS + 0.6\ OMB) / C$$

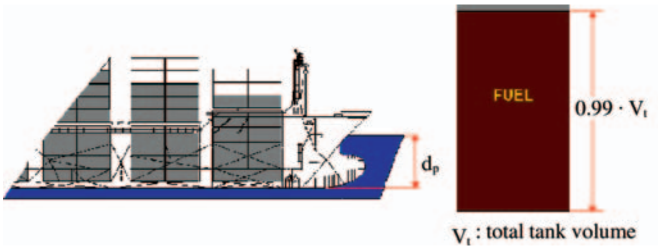

***Fig. 12.** Tank permeability calculation coefficient*

where:

OMS = mean outflow for side damage [m^3]
OMB = mean outflow for bottom damage [m^3]
C = total fuel oil volume.

⇨ For bottom damage, independent calculations for mean outflow shall be done for 0 m and 2.5 m tide conditions, and then combined as follows:

$$OMB = 0.7\ OMB(0) + 0.3\ OMB(2.5)$$

where:

OMB(0) = mean outflow for 0 m tide condition, and
OMB(2.5) = mean outflow for minus 2.5 m tide condition [m^3].

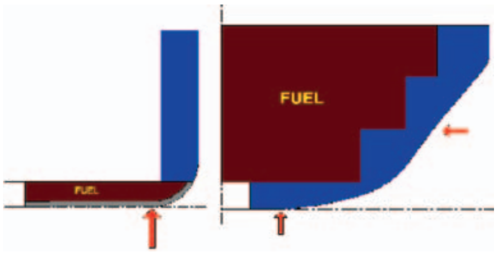

***Fig. 13.** Location of "calculated" damages*

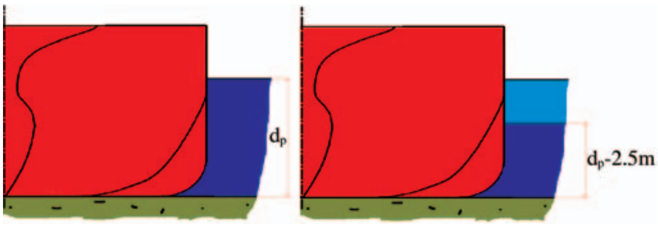

***Fig. 14.** Influence of rise- of- tide change*

CALCULATIONS OF THE MEAN OIL OUTFLOW COEFFICIENT (O_M) FOR SINE 202 SHIP

In order to perform the calculations in question a calculation sheet was elaborated by means of which the mean oil outflow coefficient (O_M) for the considered ship both before and after modification of its fuel oil tanks, was determined. Results of the calculations are given in the Tab. 1. below.

***Tab. 1.** Results of calculations of the mean outflow coefficient for SINE 202 ship*

SINE 202	O_M (permissible)	O_M (determined)
Before modification	0.01478*	0.01051
After modification	0.01477*	0.01497

* the permissible values calculated separately for the fuel oil double bottom tanks and deep tanks.

SUMMARY

- On the basis of the performed analysis it can be stated that after the modification of fuel oil tanks and application of protective coatings the mean oil outflow coefficient (O_M) has become worser as compared with its value before the modification.
- However its deviation from the permissible value is so small that it may be reduced by introducing minor changes in tank construction, e.g. a greater depth of protective coating.

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Photo: C. Spigarski

POLISH MARITIME RESEARCH Special Issue 2008; pp. 31-34
DOI: 10.2478/v10012-007-0075-0

Advanced coating of Tank Interior as means of Rising Environmental Safety of Tankers/RIM technology

Janusz Datta
Józef T. Haponiuk
Gdańsk University of Technology

ABSTRACT

The application of Reaction Injection Molding (RIM) technique for forming an elastic polyurethane coating that displays selected strength characteristics, and chemical and thermal resistance is described. The study was conducted on technical-scale using a mixing-dosing device that allowed direct dosing of liquid polyurethane system into the steel bulkhead, onto the steel surfaces, and the formation of polyurethane coating. Hard coating formed after polymer gelation and crosslinking. The elaborated technology also allowed joining of ceramsite concrete which resulted in the sandwich costruction consisting of steel, concrete and polyurethane.

Keywords: polyurethane elastomers, RIM, applications

INTRODUCTION

Reaction Injection Molding (RIM) method used in this study allows the fast forming of objects from the liquid reactive components of low viscosity. Low viscosity of the reaction mix allows for obtaining the objects under low pressure (from 5 to 8 bar) at the temperature most frequently ranging from 60 do 90°C. The increase in temperature during the process is advantageous because it results in up to even 20-fold lower energy use. It is possible to produce large objects in short production cycles, and to automate the process. RIM methos allows forming of polyurethane products that have significantly different properties which results from varying composition of the used components, interfering into the reactions, introduction of fillers, and foaming of material. Therefore it is possible to obtain solid as well as microporous materials. It is of great value that there are no byproducts and low volume of scrap produced in the reaction; scrap generation depends on how many times the system is poured onto the mold as each such operation results in 200g of waste. Therefore it is advantageous to use continous pouring in multi-mold casting apparatus (for example, of centrifugal type) because the scrap volume in relation to the produced objects is negligable. Each reactive injection process consists of a number of unit operations, e.g. preliminary mixing, storage, dosing, mixing proper and mold casting.

Mixing-dosing device used with RIM method consists of characteristic subunits that are presented in Fig. 1.

In low-pressure apparatus the metering pumps (e.g. Viking) are used that secure the required accuracy of dosing for specific components (ca. 0.5%). The highest precision of dosing is obtained for constant viscosity and identical mass ratio of components in the reaction mix. The obtaining of polyurethane elastomers can be achieved via one step or two

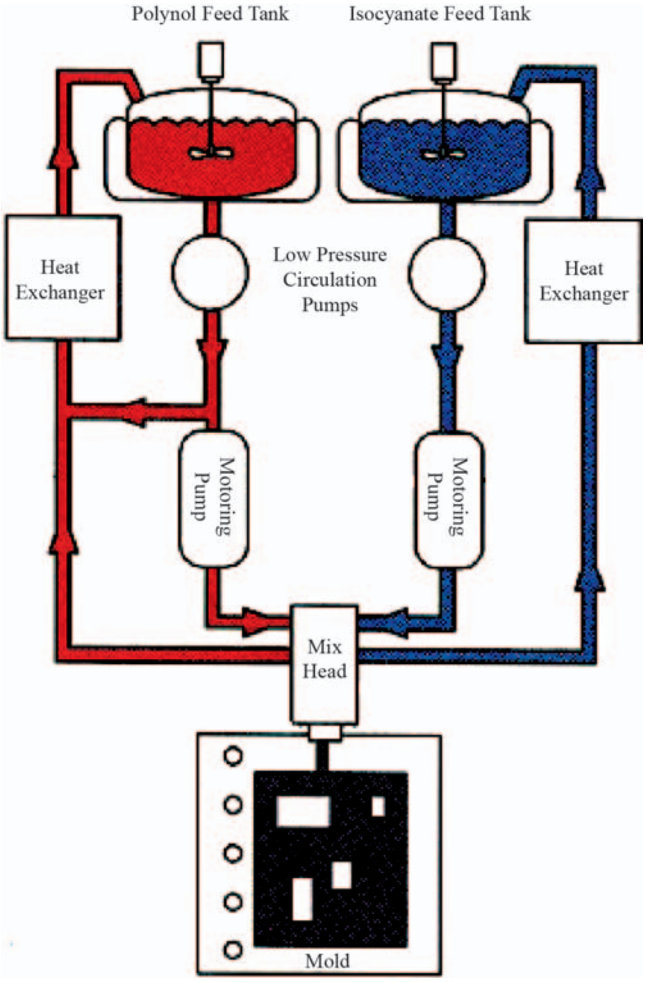

Fig. 1. Schematic presentation of mixing-dosing device [7]

step (prepolymer) method. The two step method usually allows for producing the objects with better properties; step one is the synthesis of prepolymer. Stochiometric ratios are chosen in such a way as to retain a small surplus of diisocyanate groups (Fig. 2) in relation to oligomerol. Thus the chains in the obtained prepolymer have terminal –NCO groups. Chemical stability of such semiproduct amounts to couple hours at 80-95°C, and to a week at 0°C. The addition of stabilizers, e.g. orthofosforic acid, can extend the stability. Too long storage of prepolymer at high temperature results in chain degradation, and that in turn leads to worsening of mechanical strength characteristics of the obtained elastomers.

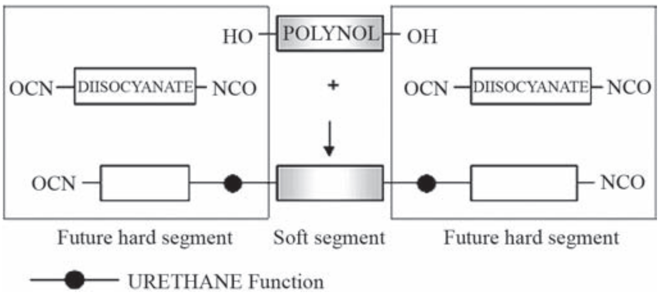

Fig. 2. *Schematic presentation of urethane prepolymer syntesis*

The second step is the synthesis of the molded urethane elasomer. To this end, the obtained prepolymer is extended with the small-size molecules of glycol or diamine. The mixing of components is performed by means of the mix head turbine of the mixing-dosing device. Mixing time usually amounts to couple seconds. The obtained clear polyurethane system is dispensed into the steel molds. After gelation and preliminary hardening, the material undergoes crosslinking at raised temperature, and next, it is molded. The RIM technology is a specific type of polyurethane system processing. The advantage of RIM (low pressure type) over the traditional injection molding of different polymers lies in the low viscosity of the material used. A comparison of the aforementioned technologies is presented in Tab. 1.

Tab. 1. *Comparison of parameters used in the processing of polyurethane systems and thermoplasts [1]*

Parameter		RIM	Injection molding
Temperature of [°C]	reagents	≈ 60	200 ÷ 300
	mold	≈ 70	room temperature
Injection pressure [MPa]		< 40	70 ÷ 150
Closing force [Pa]		0.3	60 ÷ 130
Viscosity of material [Pa·s]		0.01-1	$10^2 \div 10^5$

EXPERIMENTAL PART

Materials

4,4'- diphenylmethane diisocyanate (MDI), liquid, filter-purified, manufactured by Borsdochem (Hungary); oligo (ethylene-butylene adipate) (POLES 55/20) molecular mass 2000, manufactured by Organika - Zachem S.A. (Poland); butylene glycol (BDO) manufactured by BASF (Germany); 1,6-hexanediol (HDO) manufactured by Du Pont, (USA); 1,3-propanodiol, manufactured by POCh (Poland); ethylene glycol (GE), manufactured by POCh (Poland); oligo(oxyethylene)diol (PEG 300) manufactured by Aldrich-Chemie (Germany); orthophosphoric acid manufactured by POCh (Poland); carbodiimide, anhydric agent manufactured by Sigma Aldrich (Germany).

Catalysts: 1,4-diazabicyclo[2.2.2]octane (DABCO) manufactured by Hondry–Hüls (Germany); potassium acetate (KAc) manufactured by POCh (Poland); sodium hydroxide (NaOH) CIL bonding agents.

Bonding agents: Tixon 405 (T), Cilbond 45SF (C), Epoxid (Ep).

Measurements

The measurements of steel surface roughness were performed using a Taylor Hobson Surtronic 10 meter gauge. The analyses were conducted at 7 points on the surface of 100x10x2 mm dimension, at room temperature. A measurement consisted of a surface scan and the reading of the roughness parameter R_a. The parameter R_z was calculated on the basis of R_a value.

Tensile elongation of polyurethane samples was assessed by means of a Zwick Z20 testing machine and according to the standard procedure PN-EN ISO 527-1:1998. Testing was carried out at room temperature, at a rate of 200 mm/min and a force reaching up to 1000 N.

The polyurethane hardness was measured with an HPE Shore A durometer (Zwick/Roell) and according to the PN – ISO 868:2004 standard procedure. The following parameters were used: calibrated spring force 806.5 cN, applied force 12.5 N, 35° indenter, 25 mm path, measuring range: 0-100, type A hardness scale, accuracy ± 0.5 SHORE, and temperature ca. 22°C.

Apparatus

An EC-305 mixing-dosing device (SECMER, France); system temperature 80°C; extender temperature 40°C. The object ready for coating was kept at room temperature; prepolymer pressure 5bar; BDO pressure 5.5bar; efficiency 2.5kg/min.

Results

The application of RIM technique for producing elastic coating on the steel-concrete constructions

The chemical composition and conditions for dosing of liquid polyurethane system destined as elastic protective coating have been established. Selected parameters are shown in Tab. 2.

Tab. 2. *Conditions for the synthesis of polyurethane elastomer destined as elastic coating, by means of a EC 305 mixing-dosing device*

No	[NCO]/[OH] ratio	BDO/100g [g]	Gelation time [s]	Hardness [^{o}Sh A]
1	0.90	8.3	300	75
2	0.95	7.9	310	80
3	1.0	7.5	315	82
4	1.05	7.1	320	85
5	1.10	6.8	320	81
6	1.20	6.5	325	80

The applied study was conducted with the use of different sample models. Before each coating of the preped samples, the quality of the polyurethane system was controlled via pouring of a reference sample. sample. The reference samples had constant [NCO]:[OH] molar ratios ranging from 0.95 to 1.10; their hardness was measured directly after the heat treatment.

Fig. 3. *Polyurethane reference samples*

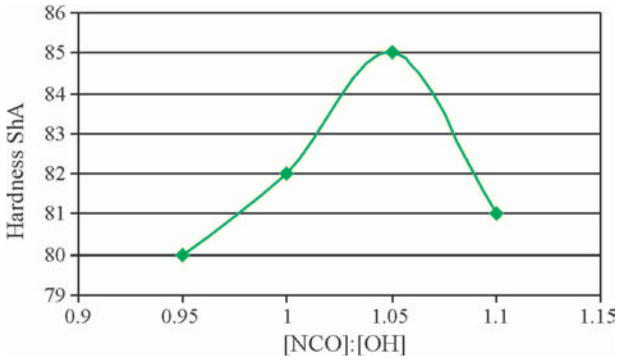

Fig. 4. *Relationship between the chemical composition and hardness of obtained PU elastomers.*

The selected polyurethane system was used to obtain layered samples for peel strength determination. Tab. 3 contains the information on how the polyurethane-steel sandwich samples were prepared for peel strength testing.

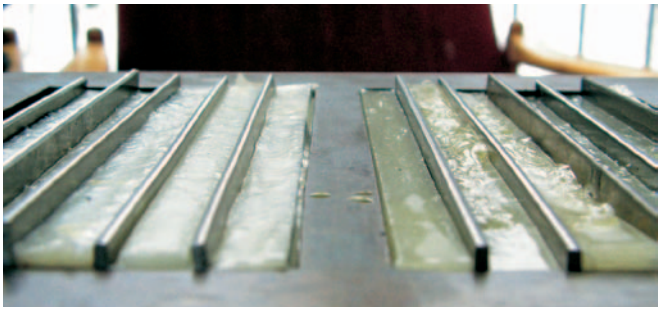

Fig. 5. *Type C samples used in studying resistance to delamination*

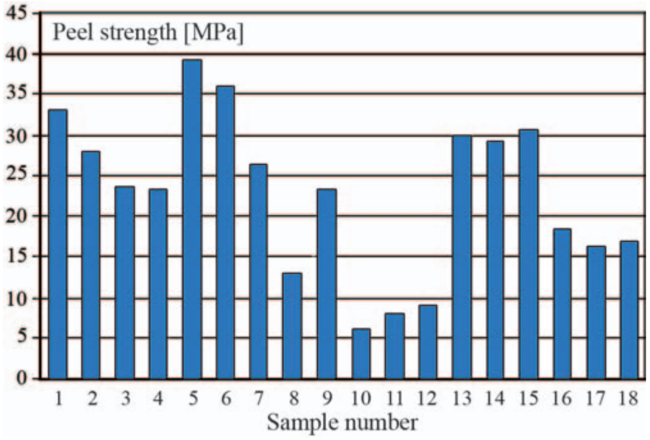

Fig. 6. *Influence of surface type and adhesive on resistance to delamination in type C polyurethane-steel sandwich samples*

Based on the data from previous studies, conducted within the same project, the task of coating the large-size samples with elastomers was undertaken in the second stage of research.

Tab. 4. *Roughness of steel surfaces coated with polyurethane*

Symbol of large-size sample	R_a [μm]	R_z [μm]
SWR 1	14.1	56.1
SWR 2	16.4	65.6
SNR*(reference sample)	0.3	1.2

Based on the obtained results, it has been confirmed that the preparation of a steel surface via abrasive blasting has a big influence on the strength of the polyuretahne-steel joining. Based on the results of testing for the susceptibility to cutting (A), tearing (B) and delamination (C), the conditions for coating of large-size steel and steel-concrete samples were elaborated. The examples of large-size steel-ceramic dumbbel samples (Figs. 5-8), used for strength testing, are shown below. These samples were used to assess the mechanical strength and the behavior of elastomer during elongation. Mechanical testing was performed using the special equipment at the Faculty of Ocean Engineering and Ship Technology, Department of Ship Manufacturing Technology, Quality Systems and Materials Science, Gdansk University of Technology.

The results of the conducted studies allowed for optimization (in reference to gelation time and temperature of the system) of the procedure for coating the main reseach object with the elastomer layer. The polyurethane system under specific conditions was low-pressure sprayed with the mixing-dosing device onto the steel construction that contained concrete coated with an epoxy resin.

Tab. 3. *Conditions for obtaining polyurethane-steel sandwich samples (C) to be used in the peel strength testing.*

Sample symbol	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Adhesive	-	-	-	Ep	Ep	Ep	T	T	T	-	-	-	Ep	Ep	Ep	T	T	T
Mechanical treatment	C*	C	C	C	C	C	C	C	C	-	-	-	-	-	-	-	-	-

*C- corundum

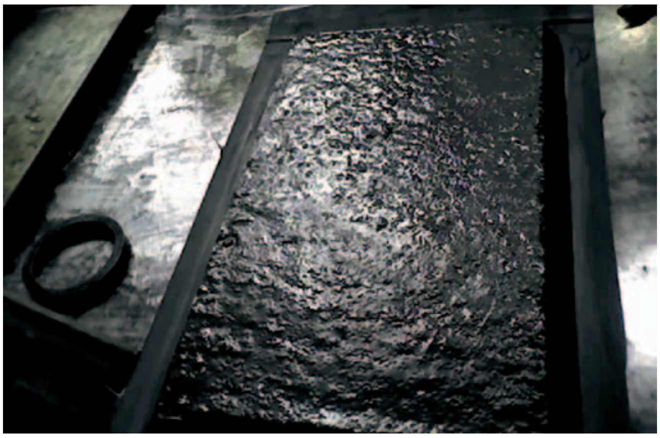

Fig. 7. Ceramic-coated sample inside the steel mold before the application of polymeric layer. Ceramic surface unpreped

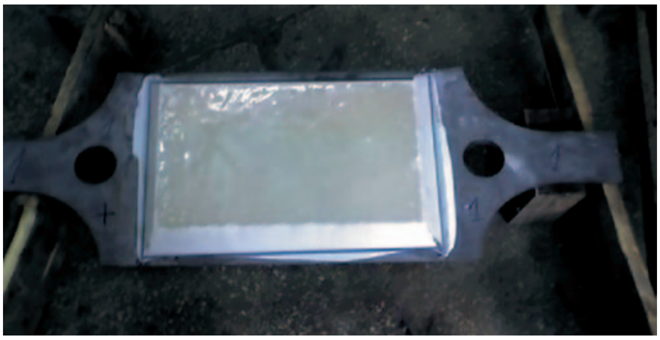

Fig. 8. Sample coated with polyureathane via RIM technique to be used for mechanical strength testing

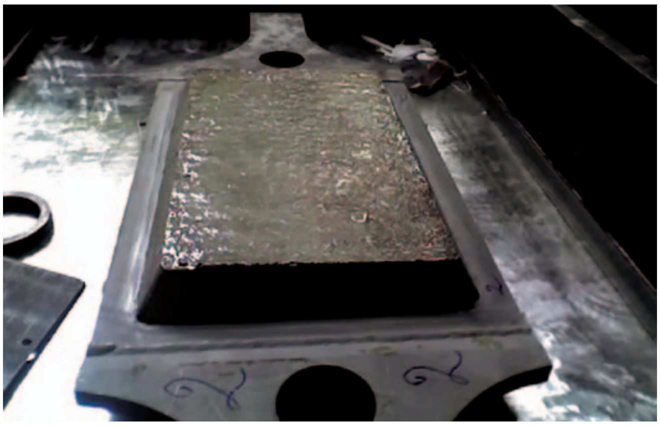

Fig. 9. Ceramic-coated sample inside the steel mold before the application of polymeric layer. Ceramic surface has been preped

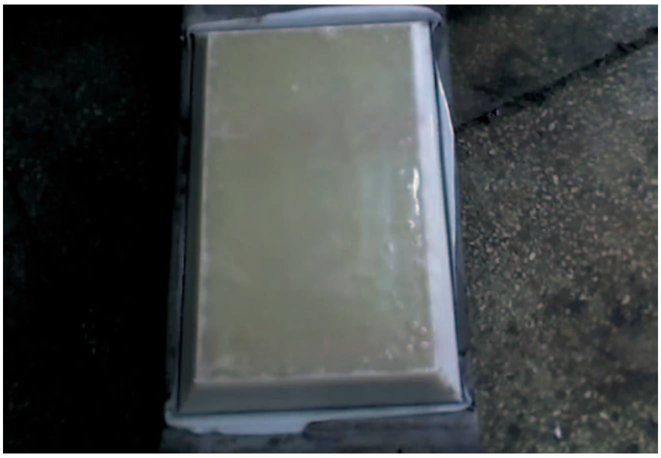

Fig. 10. Sample coated with polyureathane via RIM technique to be used for mechanical strength testing

The technology developed by us for applying the polyurethane protective coating does not employ adhesives to join polyurethane with a ceramic material. It only makes use of the high roughness of the concrete surface. The preliminary heating of the research object has not been applied either.

SUMMARY

The elaborated technology for coating the steel-concrete sandwich constructions with polyurethane elastomer via RIM method allows direct forming of the elastic layer on a given object. The produced coating has specific mechanical strength and chemical resistance. The polyurethane system applied to various surfaces (e.g. steel, concrete) by means of a mixing-dosing device allows for obtaining layers of specified thickness that properly adhere to the substrate.

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Elastomer layer on the steel-concrete object

POLISH MARITIME RESEARCH Special Issue 2008; pp. 35-41
DOI: 10.2478/v10012-007-0076-z

Results of acoustic emission tests of corrosion protection degree of ship steel tanks covered by means of protective coatings

(Phase I)

Henryk Bugłacki
Piotr Eichert
Gdańsk University of Technology

ABSTRACT

This paper presents methods and results of the 1st series of tests of acoustic emission (AE) signals, aimed at assessing degree of corrosion protection of a tank made of hull structural steel, protected by means of a protective coating combined from polyurethane layer and concrete filler. The tests were carried out in compliance with a method specially elaborated for application to the work in question. In the method were used requirements of the standards in force, as well as experience gained during realization of the research project CORRSHIP, included in 5th Frame Program of European Union. The application of the AE method to detect and localize corrosion sources during exposure of specimens to corrosive mixture confirmed its high usefulness for the carried-out tests on corrosion protection effectiveness of new types of protective coatings.

Keywords: protective coatings, ship tanks, corrosion, acoustic emission

INTRODUCTION

The tests carried out in the laboratory of the Department of Ship Technology, Quality Systems and Materials Science, Gdańsk University of Technology, were aimed at effectiveness assessment of corrosion protection of a new protective coating based on polyurethanes, as well as at finding possible corrosion sources on steel specimen surface under the combined *polyurethane layer-concrete filler* coating. The tests were performed with the use of instruments and software of the firm Vallen Systeme GmbH [9]. During the tests AE signals generated by corrosion processes on specimen surface were recorded and analyzed. Experience gained during realization the CORRSHIP research project of 5th Frame Program of EU [8, 11] was also applied. As the tests of AE signals of specimens covered by the protective coatings constitute a new task hence specimens non-coated with the protective coating as well as those protected with standard paint coatings used to cover ship ballast tank surfaces (the reference coating), were tested in parallel for comparison. The test method which covered requirements of recognized norms, standards and rules [1, 2, 3, 5, 10] was elaborated specially for purposes of this work. The hull structural steel complying with the requirements of Ship Classification Societies [6] was used as the base for the tests.

CHOICE OF DESCRIPTORS OF AE SIGNALS

All basic parameters of AE signals are defined in ASTM and PN-EN standards [13-15]. Among classical descriptors of AE signals the following can be numbered as the most important (Fig. 1) [8, 9, 13]:

1. Number of discrete emissions, counting the AE events (ΣN); this is a basic parameter informing about activity of sources
2. The mean intensity of AE signals (U_{RMS}); a basic parameter for determination of continuous emission:

$$U_{RMS} = \frac{1}{T} \cdot \sqrt{\int_0^T u^2(t)dt}$$

where:
U_{RMS} – mean squares root
u(t) – instantaneous value of electric signal transformed from acoustic one
T – integration interval

3. Value, (ΣAE), and unit rate, ($\Sigma AE/\Delta t$), of oscillations above detectability threshold
4. Peak amplitude of discrete AE signal; the best parameter for determination of damping and mechanical failure characteristics
5. Rise, duration and decay time intervals of discrete AE signal, (τ_1), (τ), (τ_2), respectively
6. AE signal energy (area under AE signal run diagram):

$$e = \frac{1}{T}\int_0^\infty u^2(t)dt$$

7. Source localization; determination of spatial location of AE source on the basis of return time measurement performed by means of a system of sensors.

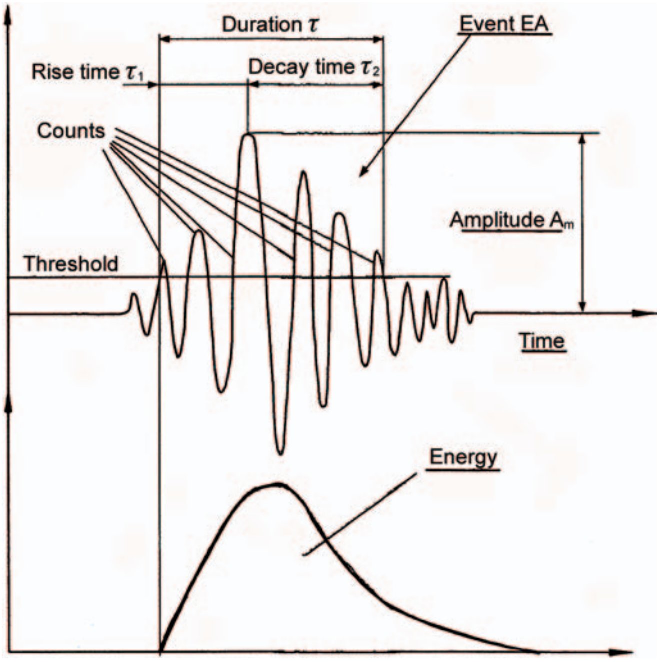


Fig. 1. *AE pulse signal parameters*

TESTING METHOD

400 mm x 300 mm x 10 mm plates of hull structural steel were covered by two kinds of protective coatings:

- Paint coating commonly applied to protect ship ballast tanks against corrosion (the reference coating),
- *Polyurethane layer - concrete filler* protective coating system.

For the tests the following number of specimens was used altogether:

- One specimen in raw state (marked „S"),
- Two specimens covered with the reference coatings (numbered : 7 and 8),
- Six specimens covered with the *polyurethane layer - concrete filler* protective system (numbered: from 1 to 6).

In Fig. 2 the specimen covered with the *polyurethane layer - concrete filler* protective system is shown.

Fig. 2. *The specimen covered with the polyurethane layer - concrete filler protective system*

As a corrosive environment 5% NaCl water solution having 20°C (±2°C) temperature was used. The corrosive solution was aerated during the tests. For the paint coatings covering steel bases and the Im3 corrosivity category for immersion in water, a long durability life equal to 3000 h (abt. 125 days) was assumed. Accelerated corrosion tests were carried out in a tank made of austenitic steel, (Fig. 3) [8, 11]. The tank was placed on a special vibration - damping foundation (foamed polystyrene, rubber plate, fibre board). The specimens were placed on insulation plastic supports in the tank.

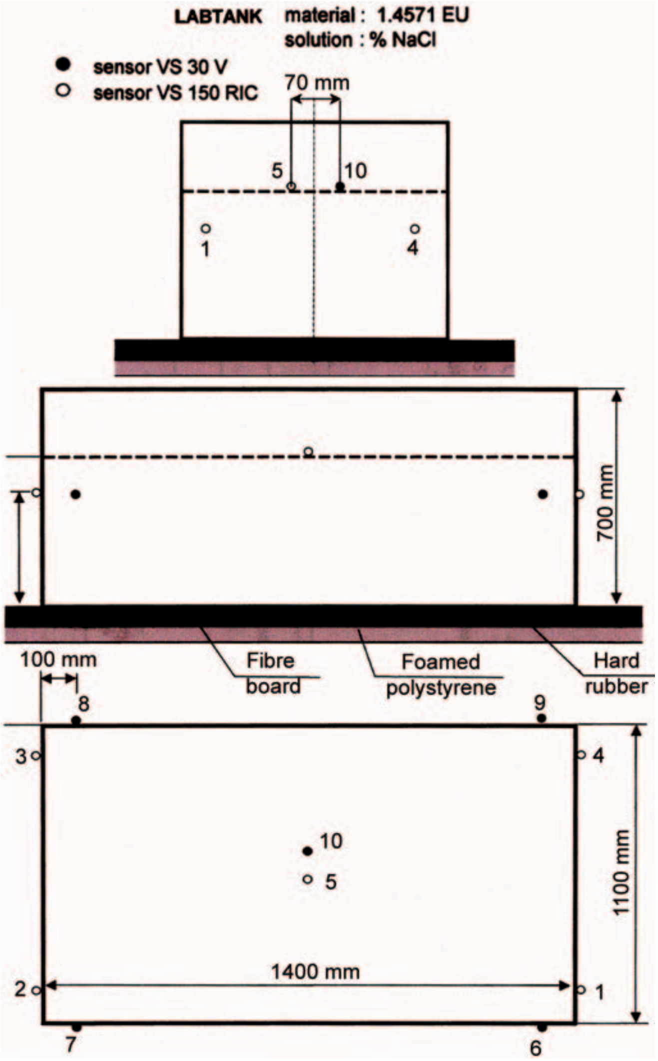


Fig. 3. *The tank for corrosion tests and arrangement of sensors*

For measurements the 16-channel set of AMSY5 system and VS30-V, VS75-V sensors of the firm Vallen Systeme GmbH (Fig. 4) were used.

Fig. 4. *AMSY5 system of the Vallen firm applicable to AE testing.*

To record AE signals and to analyze them a special software of the Vallen firm was used (Fig. 5) [8].

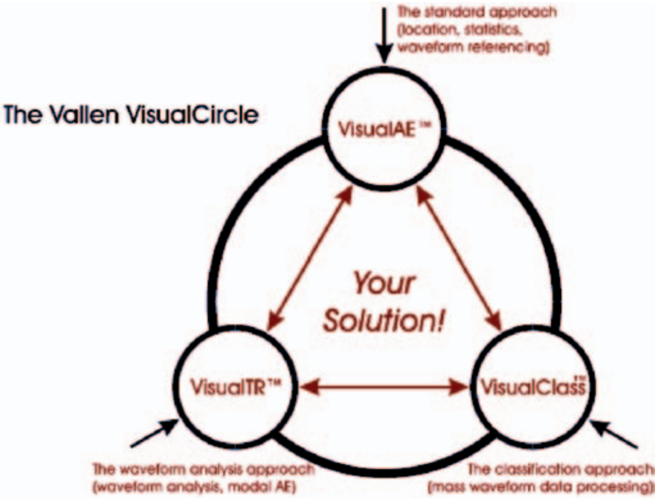


Fig. 5. *The software for AE signal recording and analyzing, of the Vallen firm [8]*

RESULTS OF THE TESTS

Into the current research program the following tests and investigations were included:

1. Localization tests and sensor sensitivity tests (graphite guide cracks –Hsu-Nilsen source); Test no. 0.
2. Background noise measurements of the tank filled with corrosive solution; Tests no. 1 through 3.
3. Localization test of the raw state specimen (the falling sphere test); Test no. 4.
4. Investigations of AE signals coming from the raw state specimen (S); Tests no. 5 through 8.
5. Investigations of AE signals coming from the raw state specimen (S) and two specimens covered with the reference paint coating (no. 7 and 8); Tests no. 9 and 10.
6. Investigations of AE signals coming from the whole set of specimens (no. 1 through 8); Tests no. 11 through 19.

Before commencing each of the tests the measurement system, setting of filters and background noise level was controlled. Assessment of localization was checked in compliance with the standard methods at the assumed values of acoustic wave propagation velocities in steel plating of the tank and corrosive solution, respectively. The obtained test-confirmed velocity values were put in the VISUAL AE program. The coordinates of the measurement sensors are presented in Tab. 1. The background noise detectability threshold was set (Tab. 2). In Fig. 6 the tank, measurement system and set of the tested specimens are presented.

Tab. 1. *Coordinates of location points of AE measurement sensors*

Type of sensor	Number	Coordinates		Type of sensor	Number	Coordinates	
		X	Y			X	Y
VS75	1	-44	-69	VS30	6	-54	-59
	2	-44	+69		7	-54	+59
	3	+44	+69		8	+54	+59
	4	+44	-69		9	+54	-59

Tab. 2. *Results of measurements of background noise level (threshold) of the tank filled with corrosive solution [dB]*

Type of sensor	Number	Background noise threshold	Type of sensor	Number	Background noise threshold
VS75	1	26.1	VS30	6	25.3
	2	23.1		7	25.7
	3	27.2		8	26.1
	4	25.3		9	28.4

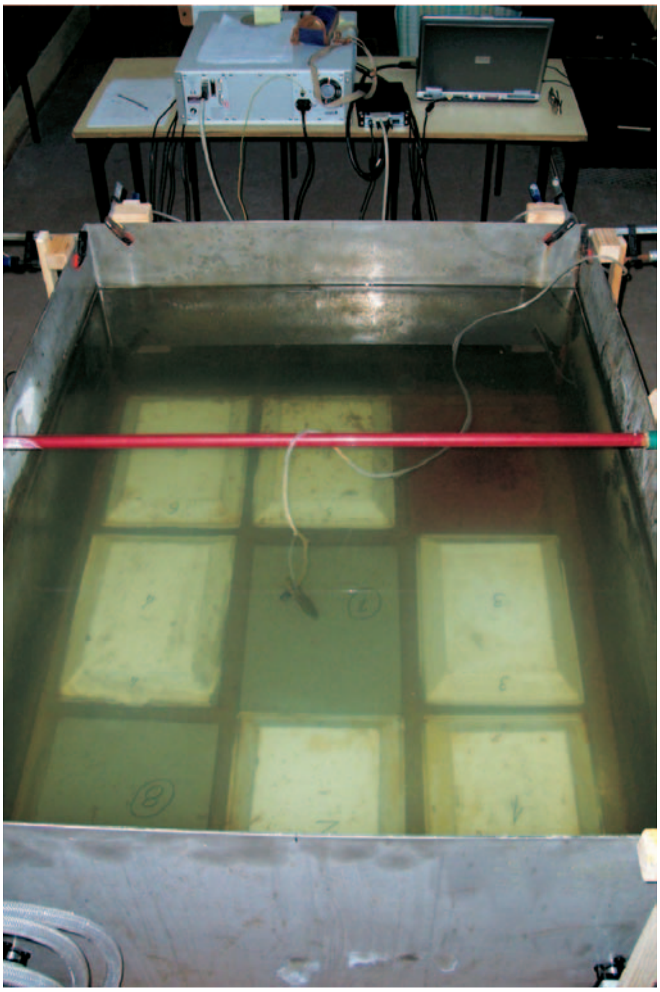
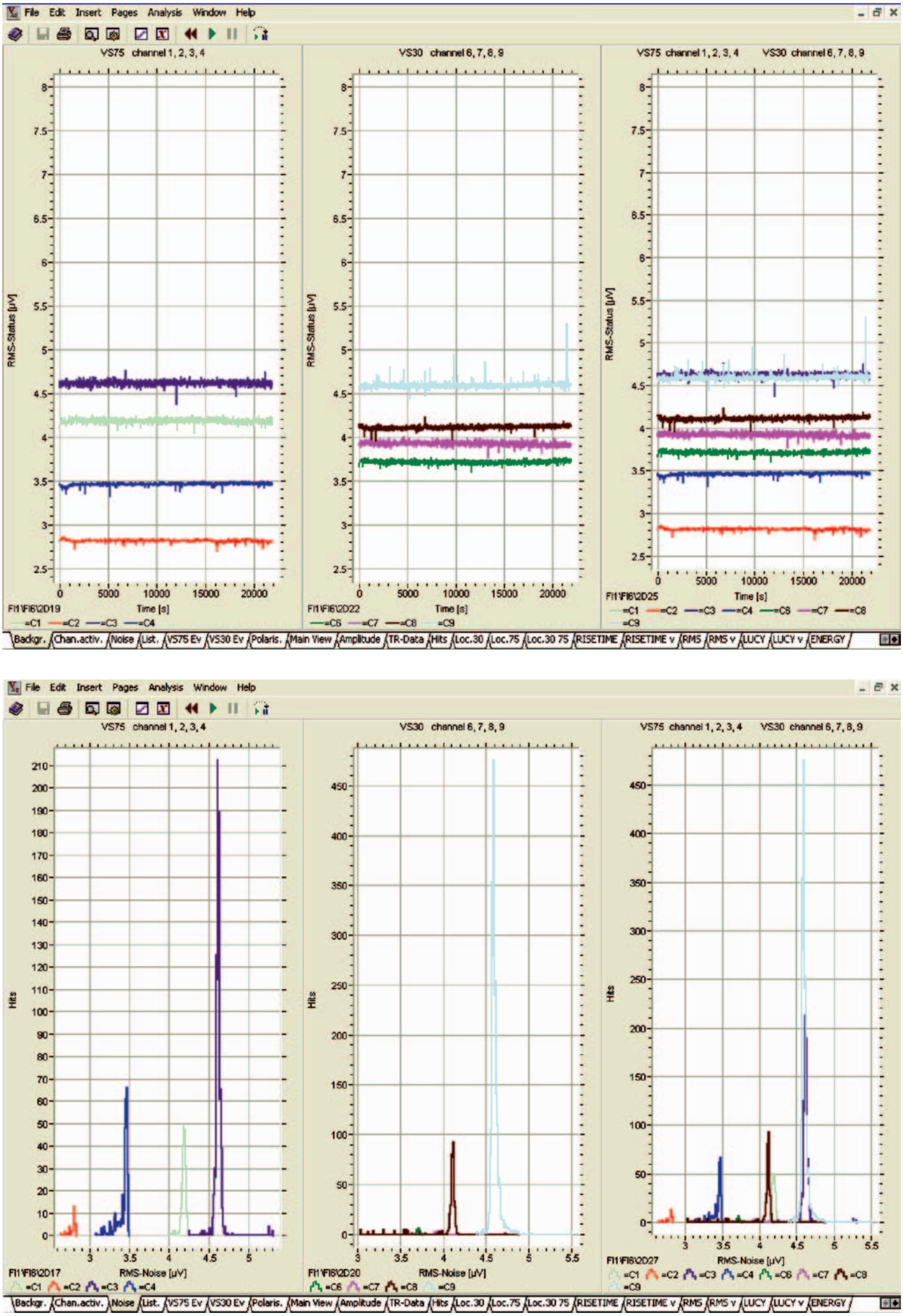


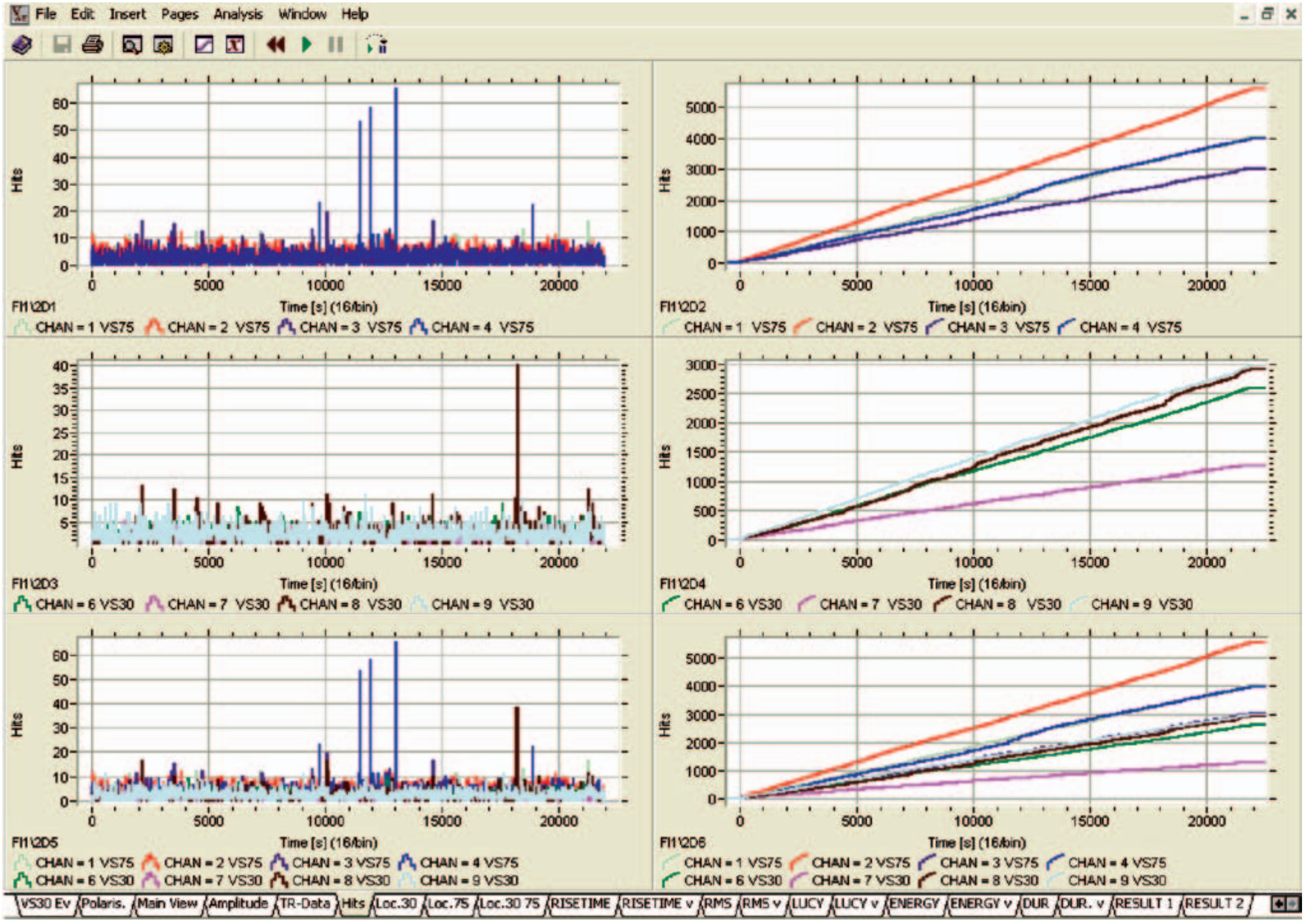
Fig. 6. *The set of plate specimens : the raw plate specimen, two plate specimens covered with the reference coating (no. 7 and 8), six plate specimens covered with the polyurethane layer- concrete filler coatings (no. 1 through 6). The spout of aeration system is visible.*

The example recorded AE signals and descriptors for the selected test no. 19 of the entire set of specimens, are presented in Fig. 7. The raw plate specimen (S) showing a significant level of AE signals has been correctly localized. The plate specimen no. 7 covered with the paint coating shows weak AE signals. Additional weak sources of AE signals, located on the plate specimen no. 6 covered with the *polyurethane layer-concrete filler* coating, were also found. As the AE signals localized in it are characterized by another quantity of energy and another rise time it can be deemed that the source of AE signals is of a different character than corrosive one. It can be e.g. processes which occur within internal structure of the concrete filler.

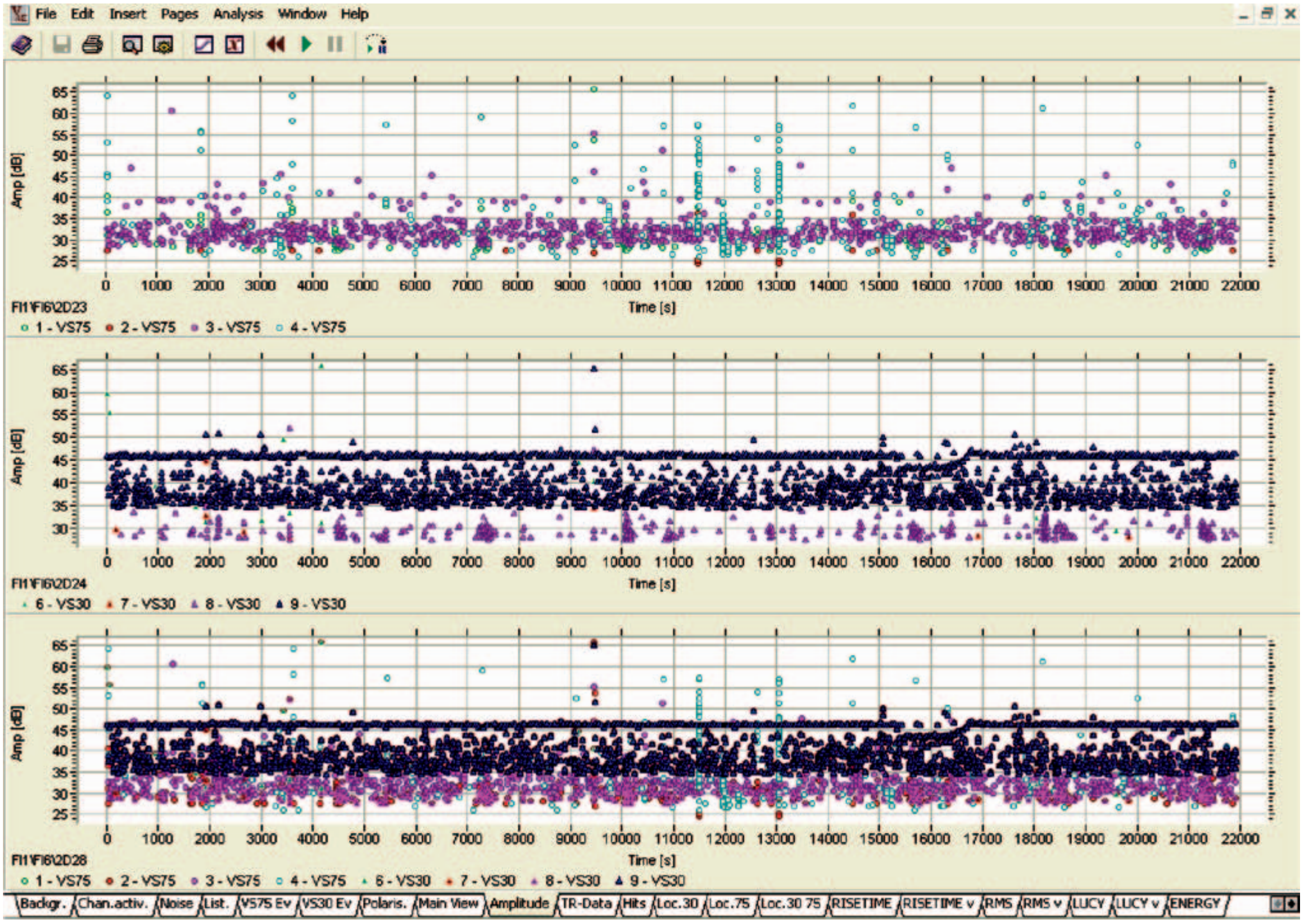
a) *The mean intensity of AE signals (background) – the background* U_{RMS}



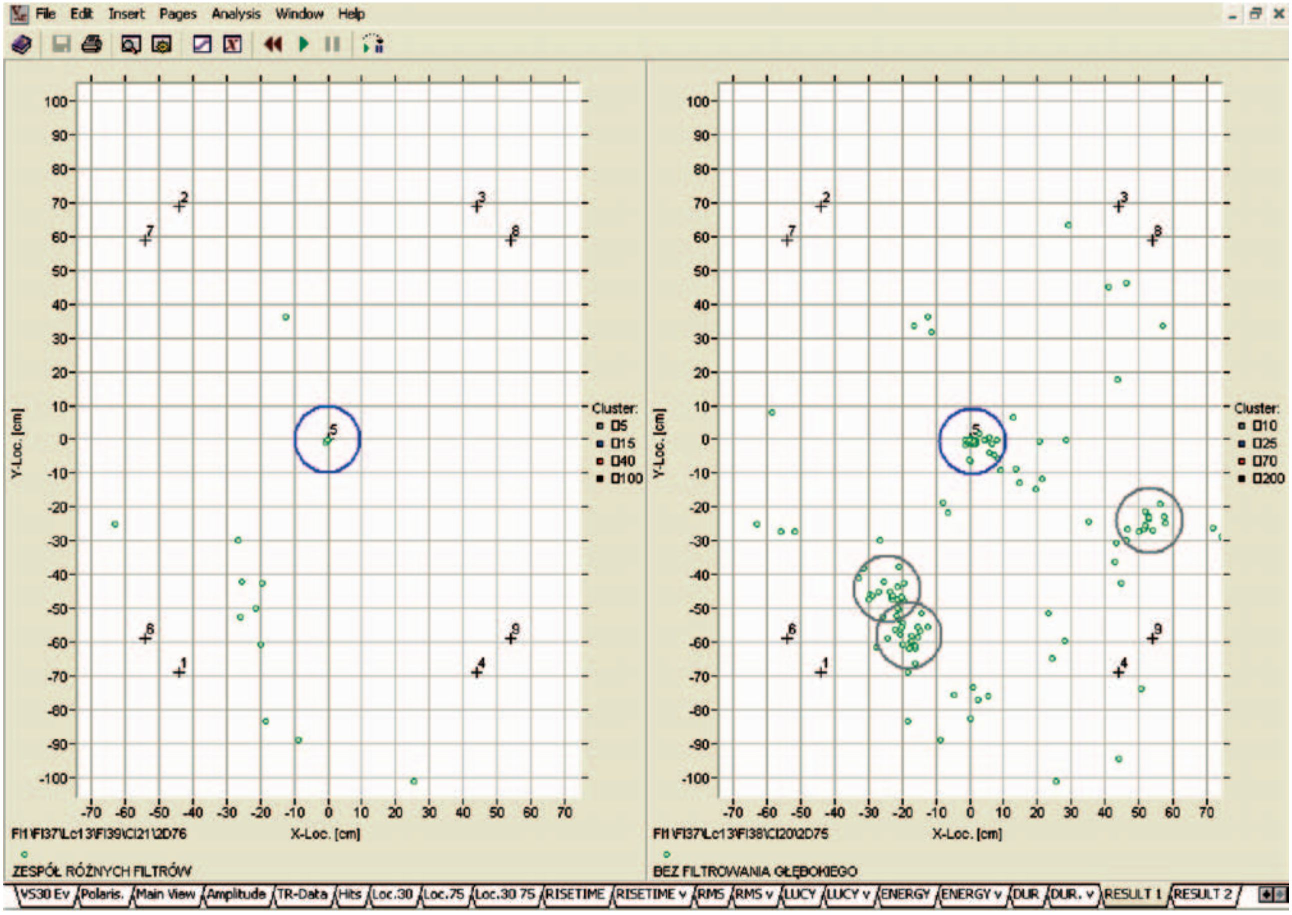
b) *The response (detection of one pulse signal in the channel) - hits*



c) *The peak amplitude A_m*



d) *Localization without filtering*



e) *Localization with filtering*

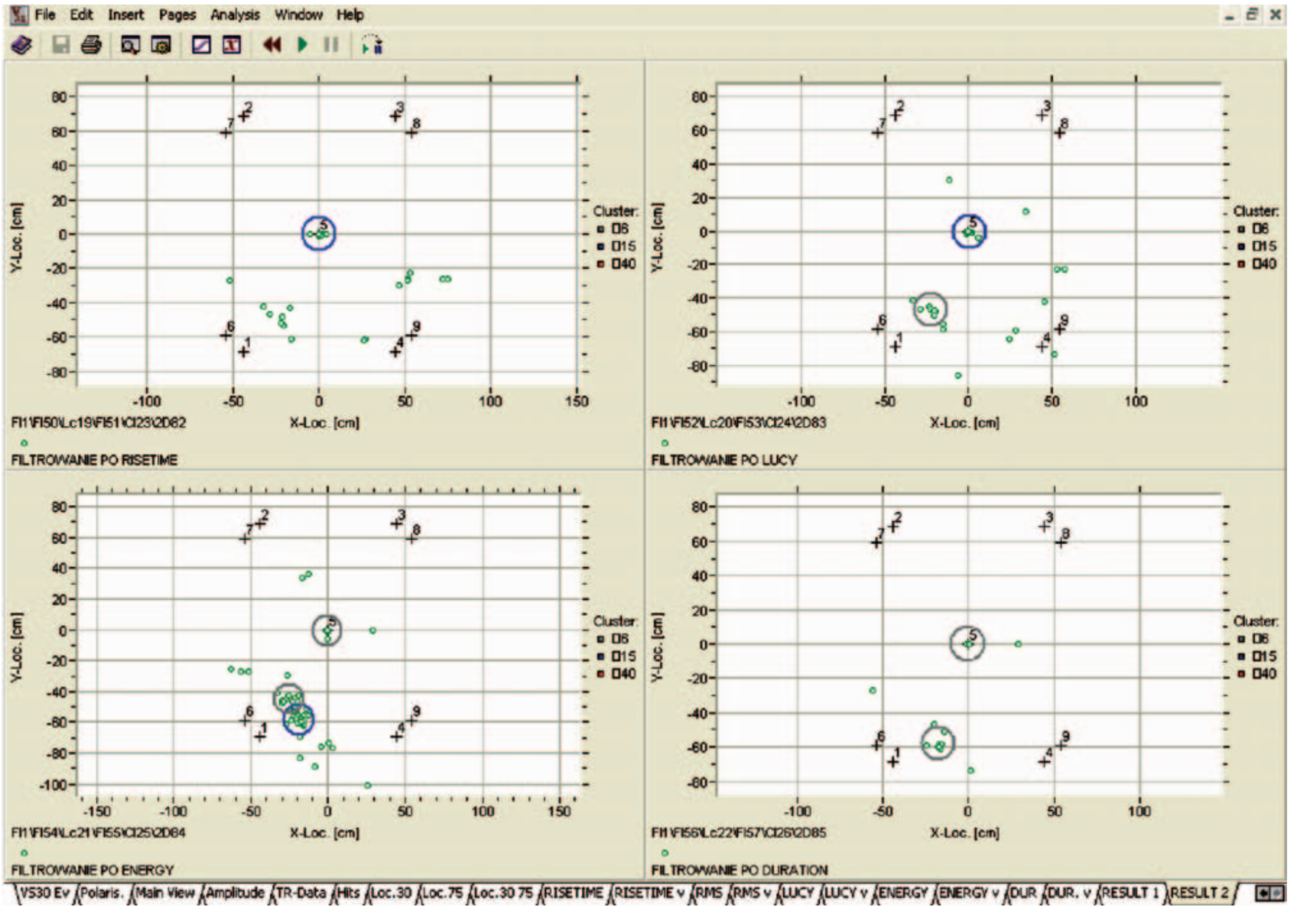


Fig. 7. *Example AE signals and descriptors recorded for the selected test no. 19 performed for the whole set of plate specimens*

SUMMARY

The application of the acoustic emission (AE) method to detect and localize corrosion sources during exposure of specimens to corrosive solution, confirmed its high usefulness during the performed tests on the assessment of corrosion protection effectiveness of new types of protective coatings.

The preliminary conclusions resulting from the 1st series of the tests are the following :

- The raw plate specimen is characterized by a significant level of acoustic emission and it was correctly localized in each case.

- The plate specimens covered with the reference coating did not show any corrosion acoustic emission during this phase of research. Small point sources of corrosion visible at the edges of the plates are characterized by a low level of acoustic emission, a few orders lower than that of the raw plate specimen.

- The plate specimens covered with the protective coating also did not show any corrosion acoustic emission during this phase of research. Small point sources of corrosion visible at the edges of the plates, are characterized by a low level of acoustic emission, a few orders lower than that of the raw plate specimen.

- Small additional acoustic emission sources localized on the plate specimen with the protective coating (no. 6) were found. The localized signals which are characterized by another energy quantity and another rise time, suggest that their origin character is different than that of corrosion processes, e.g. resulting from the cracking of internal concrete structure of coating layer.

- It is necessary to perform next series of the tests aimed at searching for corrosion processes on the plate specimens with the reference coating or *polyurethane layer-concrete filler* coating as well as to more thoroughly analyze signals coming from the plates (especially from the specimen no. 6) in order to find nature of origin of localized signals.

NOMENCLATURE

ΣN – number of discrete emission
U_{RMS} – mean intensity of signals
$u(t)$ – instantaneous value of electric signal transformed form acoustic one
T – integration interval
ΣAE – number of oscillations above their detectability threshold
A_m – peak amplitude of discrete emission signal
τ_1 – rise time interval of pulse signal
τ – duration time interval of pulse signal
τ_2 – decay time interval of pulse signal
e – pulse signal energy.

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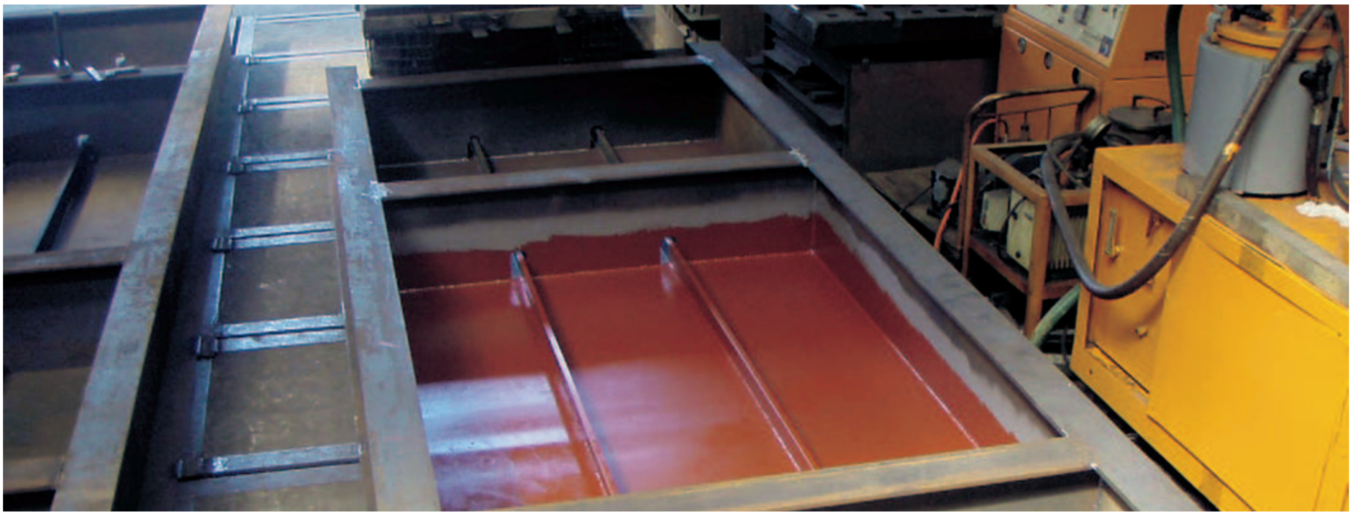

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