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CONCRETE IN CONTACT WITH CRUDE OIL PRODUCTS

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Durability analysis of RC (reinforced concrete) system by field and laboratory tests based on data collected over many years is described. All structures are situated in an environment, which can be divided into physical, chemical and physico-chemical. The problem of physico-chemical influence on the reinforced concrete is not well known. It has been found that the crude oil products with a very low neutralization number are the physico-chemical active agents affecting the concrete. Such environment is basically connected with marine and industrial structures. Experimental analysis affecting compressive strength is described. Comparing the influence of various oil products on the compressive strength of concrete leads to the conclusion that there are large differences in effects. From vaseline oil with almost no influence to some mineral oils with the serious influence, even to 30 or 50% loss of initial values. Contamination of concrete by hydrocarbons gives almost a new material, which behaves differently.

1. Introduction

The durability of concrete in different environments is now recognized as a very important part of design process. Little is known about the physico-chemical environment, which contains organic active polar molecules. It has been found that crude oil products with a very low neutralization number (lower than 0.25 mg KOH/g) include some of them. These oil products are basically connected with marine and industrial RC structures.

In technical literature, effects of crude oil products on concrete are classified either as non-harmful or only mildly harmful, but there is an evidence that serious damage can be caused. For example, an investigation into the damage to a large turbine (200 MW) at a national power generating plants in Poland concluded that the damage meant a large decrease in dynamic stiffness of the RC foundation frame caused by a heavy contamination of concrete by mineral oil.

In case of physico-chemical environment, usually physico-chemical bonds are affected and because of that the process can sometimes be reversible.

Long-term investigations were put in hand to determine the effect of a group of crude oil products - mineral oils - on properties of concrete and reinforced concrete. The paper reports our detailed findings.

2. Destruction mechanism

The influence of different crude oil products on concrete in comparison to water investigated by the author and other researchers is shown in Fig. 1.

The most common conclusion is that concrete behaves as a "molecular sieve" where different sized

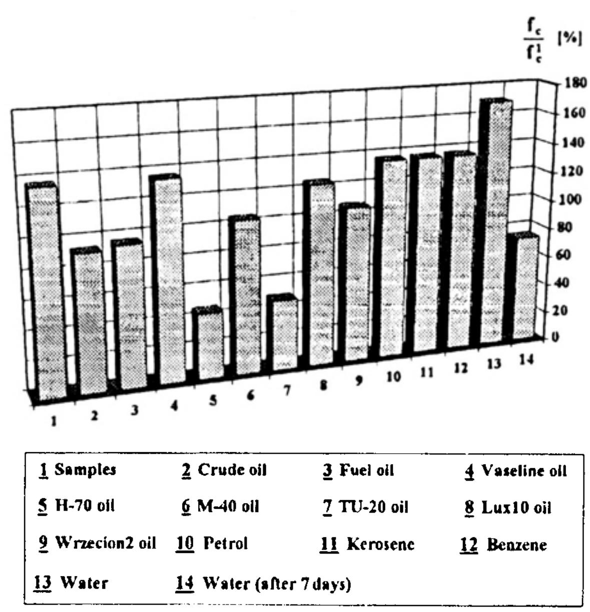

Fig. 1. Effects of different crude oil products influence on concrete (in comparison to water)

molecules penetrate differently into the concrete pore system [1]. In particular, small sized molecules as in water penetrate the smaller inner gel pores not reached by larger molecules. Cook and Haque [2] also concluded that the reason why benzene and kerosene do not cause any changes in the properties of concrete similar to those caused by water was due to the molecular sieve effect, which allowed water particles to penetrate gel pores not reached by other fluids.

Feldman [3] is less certain about the molecular sieve effect and has suggested that even fluids of similar molecular size to water such as methanol cannot penetrate pores reached by water. The ability of water to penetrate the inner layer space is attributed to its special "affinity".

Short time changes in properties of concrete saturated by water is due to lowering cement matrix strength and they are reversible (see 14 in Fig. 1). In a long term water acts positively on concrete and strengthening occurs (13 in Fig. 1) [4].

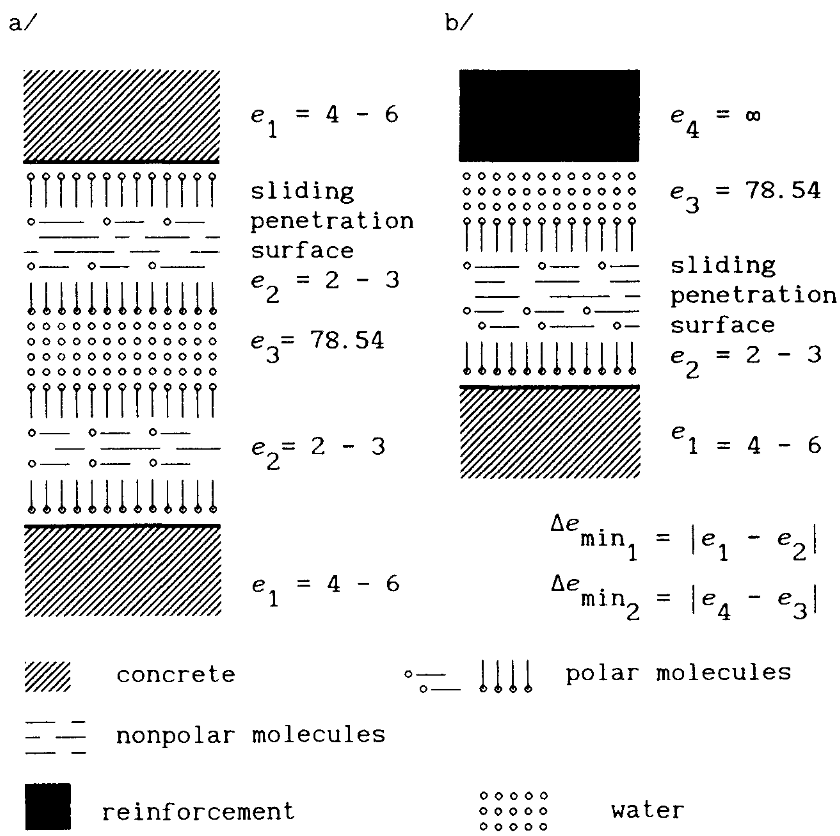

Fig. 2. Mild change of phases rule for mineral oil and water in concrete (a) and reinforced concrete (b) microcracks and microspaces

It is known that every mineral oil consists of basic oil and improvers. The basic oil is electrically almost neutral (non-polar), only the improvers are active including surface-active polar molecules.

In spaces unfilled with water, oil penetrates and deposits the polar molecules on the surfaces. When water fills these spaces, the penetration of oils takes place according to the minimum of dielectric constant e gradient as shown by Fig. 2 [5].

The mechanism of failure of the concrete inner structure and its bond to reinforcement can be explained by the effect of lowering the surface energy and by the effect, which takes place at the polar fluid-solid interface. When a microcrack has occurred, the polar molecules penetrate along its surface to the apex. Therefore, at their apexes, microcracks and other microdefects become subjected to a pressure action. The polar active molecules adsorbed on the surface give a reduction in surface energy, which can make this surface more ductile [6].

The results of long-term action of different mineral oils are presented in Fig. 3. They clearly show the significant decrease of concrete C-25 compressive strength in time [7].

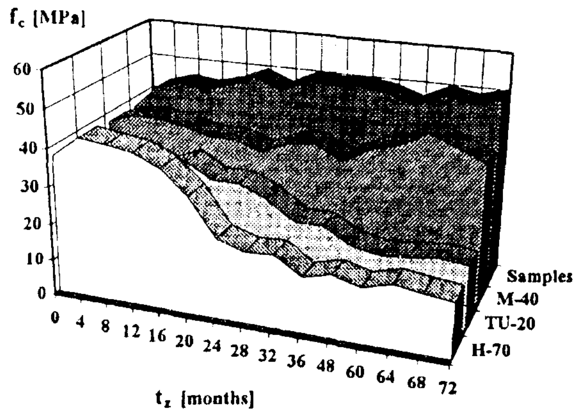

Fig. 3. Variation of concrete C-25 compressive strength during the period of exposure to different oils

Contamination of concrete by hydrocarbons gives almost a new material, which behaves differently. The results of the stress (σ) - strain (ε) relation in dry state and in fully saturated in function of the longitudinal strains are different. The nonlinear behaviour of strength and strain variations depends on the contents of hydrocarbon and its type. The schematic graph of the σ - ε relation for dry and for oil saturated concrete is shown in Fig. 4a; it can be noticed that the strain ε_R, corresponding to the maximum stress, is lower for oil saturated concrete than for dry concrete; on the other hand, the maximum limit strain ε_m is correspondingly higher. Figure 4b presents a real graph for dry and oil TU-20 saturated concrete C-25.

Comparison of physico-chemical influences between water and oils leads to a conclusion, that polar molecules within the hydrocarbon chain are harmful. Water molecules are small dipoles geometrically and when they act positively on concrete strengthening occurs. The hydrocarbon chain is non-polar and non-harmful, but in connection with hydrophilic part gives the problem. That's why petrol, kerosene, benzene and vaseline oil are not corrosive to concrete since they contain non-harmful short hydrocarbon chains. First of all water in fuels is the polar element or there is a very small part of other polar molecules, but with very short chains, which are not long enough for hydrophobing the concrete inner structure.

The existence of organic polar active molecules in liquids may be detected directly by IR spectroscopy. The degree of polarization of mineral oil can be measured also indirectly by its lubricity or demulgation method.

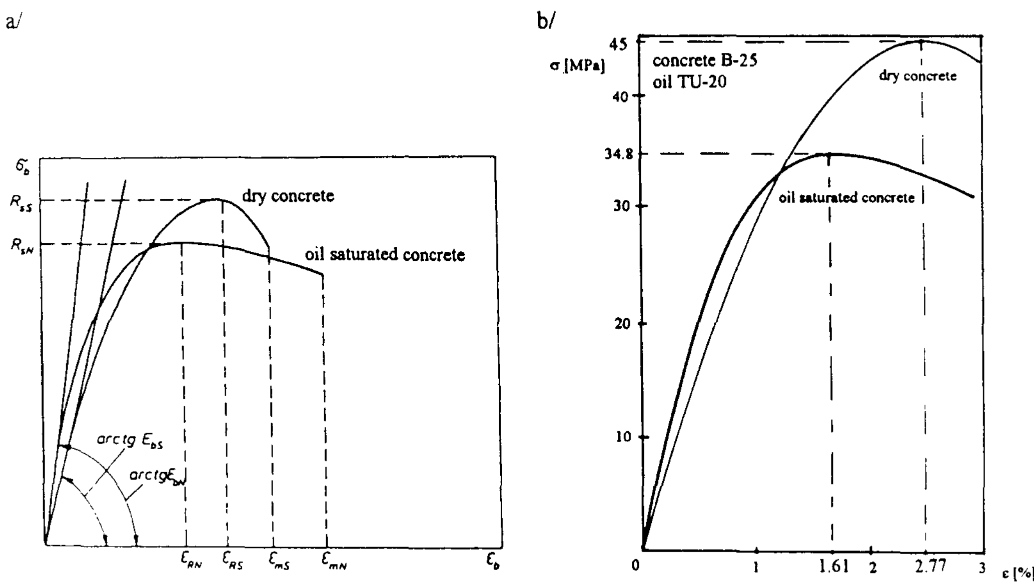

Fig. 4. σ - ε diagram for dry and oil saturated concrete
a/ schematic proposal, b/ real graph for oil TU-20 and concrete C-25

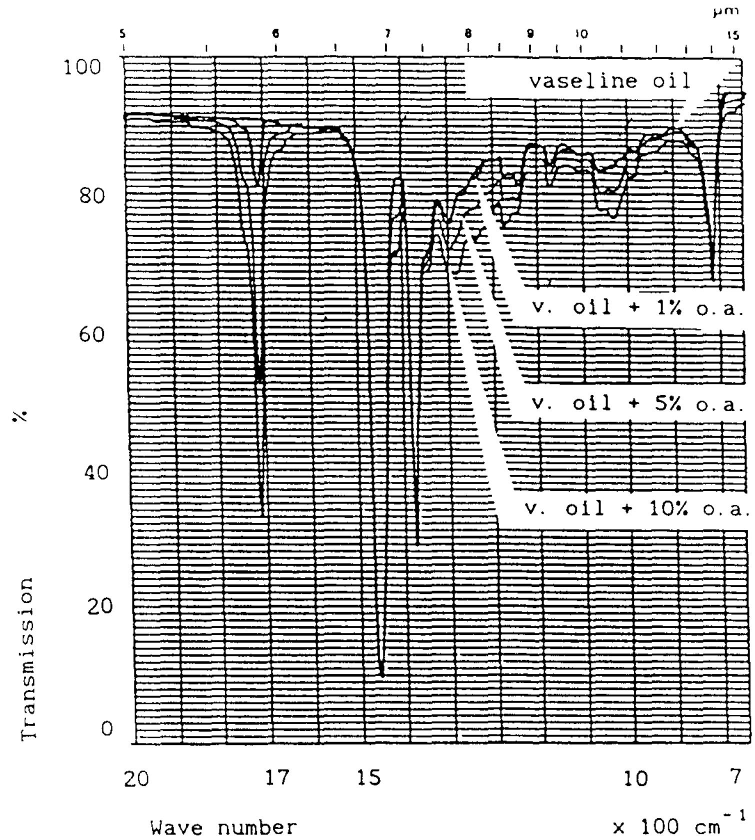

Fig. 5. Comparison of vaseline oil IR spectra with the spectra of other mixtures

3. Assessment methods

Using the infra-red spectroscopy with a small amount of oil one can get the whole plot of the examined fluid. Comparing the basic oil and oil with improvers, it can be seen the significant peaks in the case of all the most active polar molecules. Figure 5 shows a comparison of vaseline oil (basic non-polar oil) IR spectra with the spectra of mixtures based on it, by adding 1%, 5% or 10% of oleinic acid (very polar active improver).

The degree of polarization of acting fluids can be also measured indirectly by its lubricity P_Z. Lubricity depends on viscosity and for statistical multiple regression analyses the kinematic viscosity η_k and the lubricity P_Z are used as dependent variables, giving a chart presented in Fig. 6. The chart can be used to find compressive strength of concrete grade C-25 after a long-term action of any crude oil products.

The simplest method is a demulgation method, which is based on assumption, that polar molecules keeping emulsion. The last figure shows the dependence of concrete compressive strength upon the water phase exuded from oil-water emulsion after 60 min.

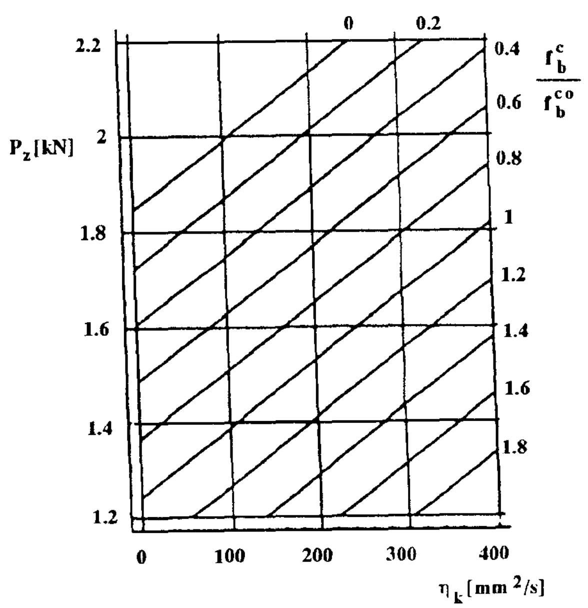

Fig. 6. Lubricity method chart for concrete C-25

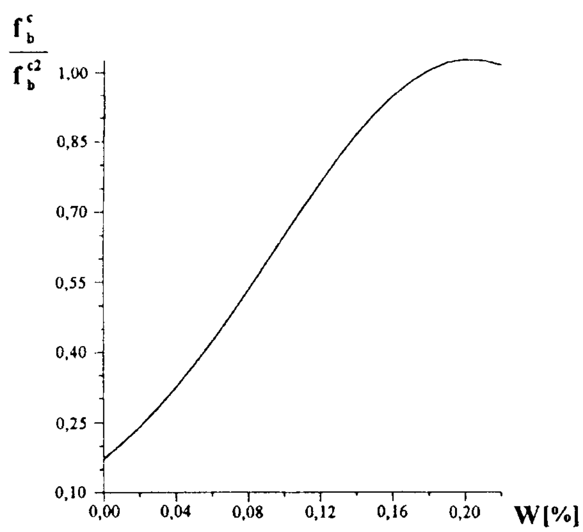

Fig. 7. Relationship between concrete compressive strength and amount of exuded water phase from demulgation method

4. Conclusions

The durability analysis of concrete exposed to a crude oil products environment shows that significant reduction in compressive strength can occur.

When designing a structure of cement constructional material in contact with crude oil products, apart from checking the value of neutralization number, checks should be made on presence of organic polar active molecules by the infra-red spectroscopy, lubricity or demulgation method. Some of the oil products are safe but some are clearly very aggressive.

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BETONO KONTAKTAS SU NAFTOS GAMINIAIS

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Santrauka

Straipsnyje pateikiami gelžbetonio patvarumo analizės duomenys, gauti iš daugiamečių stebėjimų. Visi statiniai yra tam tikroje aplinkoje, kuri gali būti fizinė, cheminė ar fizinė-cheminė. Pastarosios aplinkos poveikis gelžbetoniui mažai tyrinėtas. Tačiau nustatyta, jog naftos gaminiai su mažu rūgšties kiekiu yra fizinės-cheminės medžiagos, veikiančios betoną. Aprašomi bandymų duomenys, kurie rodo tų medžiagų poveikį betono gniuždymo stiprumui. Lyginant įvairių naftos gaminių įtaką betono gniuždymo stiprumui, galima sakyti, kad toji įtaka labai įvairi: nuo parafininės naftos, kuri beveik neturi jokios įtakos betonui, iki kai kurių naftos gaminių, veikiančių taip, kad betono stiprumas sumažėja 30-50%. Betono tarša angliavandeniliais gali sukurti beveik naują medžiagą, turinčią visai kitokių savybių.

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