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ASSESSMENT OF THE USEFULNESS OF INORGANIC SORBENTS IN THE REGENERATION OF INDUSTRIAL WATER AND GLYCOL-BASED ANTIFREEZES

Key words

Antifreezes, ageing, sorption regeneration, operating properties, heat exchanger.

Abstract

The article presents the results of tests on sorption regeneration of water and glycol-based antifreezes used in industrial installations for heat exchange. Activated carbon, zeolites, and fly ashes with high carbon content, constituting waste from a conventional power plant, were used as sorbents. The tests were carried out using a UV-Vis spectrophotometer with inductively compressed plasma and equipped with a mass detector (ICP-MS). The author also studied physicochemical properties of a regenerated liquid, i.e. its density, alkaline reserve, flow temperature, and the corrosive impact on metals. The results were then compared with the parameters of a liquid prior to regeneration and an unused liquid. A possibility to improve selected physicochemical properties of an antifreeze was also confirmed, particularly the alkaline reserve, as well as a possibility to remove, through sorption, soluble compounds containing copper and lead, and colouring compounds. The author also observed the limited corrosive impact of a regenerated liquid on metals, as compared to a liquid not subjected to sorption. The most effective sorbents were activated carbon type CWZ-14 and fly ashes with carbon content over 8% by weight.

Introduction

Water and glycol-based antifreezes are used as heat carriers in many technological areas. They are, for instance, used in engine cooling systems, industrial central heating systems (particularly in large offices and warehouses), or heat pumps in air conditioning systems. Antifreezes in the form of ready-made solutions are most common. Apart from water and ethylene or propylene glycol, theses liquids frequently contain additives that improve their functional properties, e.g. corrosion inhibitors, biocidal substances, or defoamers [1].

Water and glycol-based antifreezes age with time, which influences their technological and ecological characteristics [2]. Such substances are particularly subjected to oxidation, and the products resulting from this process induce corrosive electromechanical impacts that take place in micro cells and are formed on the surface of structural elements made of, e.g., steel, copper, or aluminium alloys [3, 4]. It is also worth noting that structural materials or the oxide products of their corrosion can catalytically influence oxidation of glycol, which increases the number of acidic products, and intensifies corrosion, negatively influencing proper operation of a heat exchange system [5]. Therefore, increasing the reliability of such a system can be obtained through cyclical regeneration of an antifreeze used. There are filtration technologies that enable treatment of such substances. They particularly help one to remove solid pollutants resulting from external precipitation, corrosion, or liquid ageing [6]. Nonetheless, it is essential to include single operations that enable the removal of acidic products of glycol ageing, as well as other soluble products, e.g., those that give a liquid a brownish colour, which disqualifies the product on marketing grounds. Adsorption of resulting products from water and glycol-based antifreezes on selected inorganic sorbents, like zeolites or activated carbons, can be an effective method of regeneration. An interesting kind of sorbents are also fly ashes from the combustion of a carbon ash in conventional power plants that can be used for, e.g. wastewater purification [7, 8].

The aim of the research was to assess the usefulness of selected inorganic sorbents for the regeneration of water and glycol-based antifreezes used in industrial cooling systems, while the expected result was to increase the alkaline reserve with liquid discolouring, simultaneously maintaining other important performance characteristics at a level that guarantees reliable operation of a heat exchange installation.

1. Research methodology

The author selected several types of inorganic sorbents that differed in terms of their chemical composition and spatial structure influencing expansion of the contact area. The experiments were conducted using activated carbon with alkaline reaction (CWZ-14 and CWZ-22 by Elbar Sp. z o.o.), zeolites, and fly ashes with different carbon content, constituting waste from conventional power plants. Figure 1 presents microscopic images of sorbents that were taken with an electron-scanning microscope.

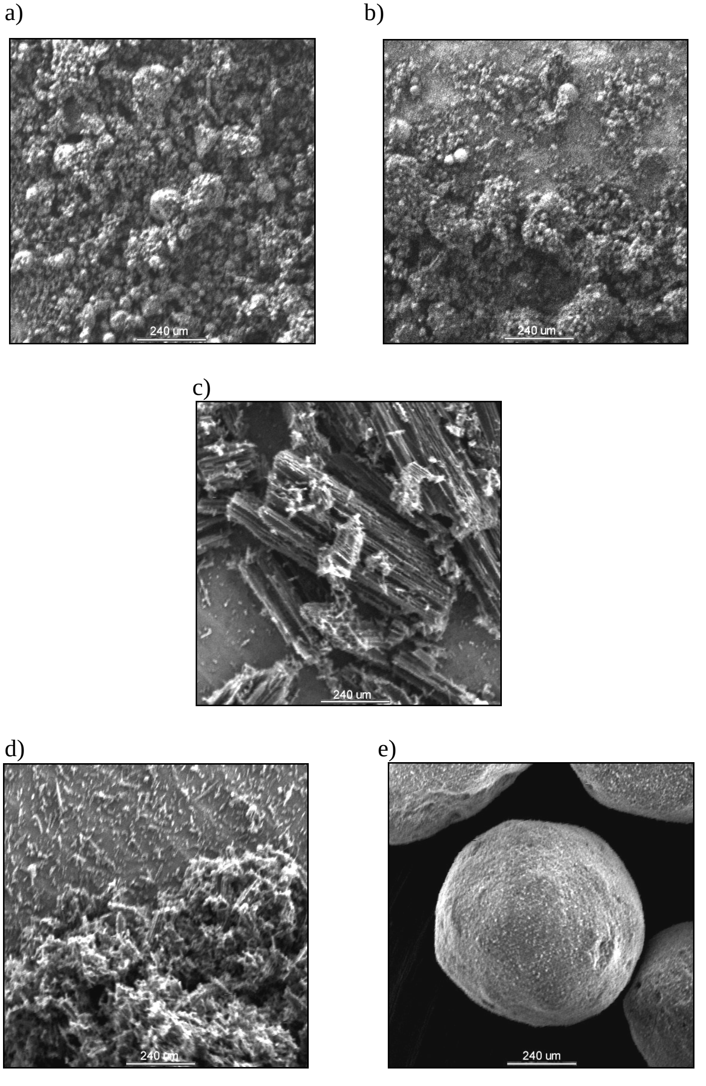

Fig. 1. SEM images (magnification 100x) of structures of selected sorbents: a) fly ash containing 8.18% of carbon, b) fly ash containing 18.88% of carbon, c) activated carbon CWZ-22, d) activated carbon CWZ-14, e) zeolite

Samples of liquids after the initial mechanical filtration were contacted with each sorbent. The author used 2 g of a sorbent per 100 g of a liquid. The description of samples subjected to further testing is presented in Table 1.

Table 1. Identification of antifreeze samples subjected to treatment employing different types of sorbent materials

Sample symbol	Characteristics
CN	Water and glycol-based antifreeze before use
CR	Filtered antifreeze used in a heat exchange installation for the period of three years
CR+LP8,18	Liquid after filtration subjected to sorption using fly ashes containing 8.18% carbon by weight
CR+LP13,13	Liquid after filtration subjected to sorption using fly ashes containing 13.13% carbon by weight
CR+LP18,88	Liquid after filtration subjected to sorption using fly ashes containing 18.88% carbon by weight
CR+WA14	Liquid after filtration subjected to sorption using activated carbon type CWZ-14
CR+WA22	Liquid after filtration subjected to sorption using activated carbon type CWZ-22
CR+Z	Liquid after filtration subjected to sorption using zeolites

After sorption, the samples of a regenerated liquid were subjected to colorimetric analysis employing a UV-Vis spectrophotometer by Jasco (the wavelength range between 400–750 nm using a 1 cm quartz cuvette) and spectral tests employing a spectrometer with inductively compressed plasma and equipped with a mass detector (ICP-MS). The samples subjected to the latter analysis first underwent microwave mineralization in nitric acid, which allowed the determination of the total content of the elements present in the sample. The measurements were taken with the iCAP-Q instrumentation by Thermo Scientific in which a collision chamber powered by helium is used. The additional tests conducted included physicochemical analyses concerning the liquid density at 15ºC (according to PN-EN ISO 12185:2002), the alkaline reserve (PN-C-40008/05:1993), the flow temperature (PN-ISO 3016:2005), and the corrosive impact on metals (PN-C-40008/07:1993). The author used the following devices for the above-listed tests: the DMA 4500N by Anton Paar for density measurements, the Mettler DL20 titrator for alkaline reserve measurements, the CPP 5Gs by ISL for flow temperature measurements, and the laboratory set for corrosive impact analyses as specified by the standard.

2. Research results and their analysis

2.1. Spectral analysis of antifreezes

The results of colorimetric analyses of antifreeze samples after sorption are presented in Figure 2.

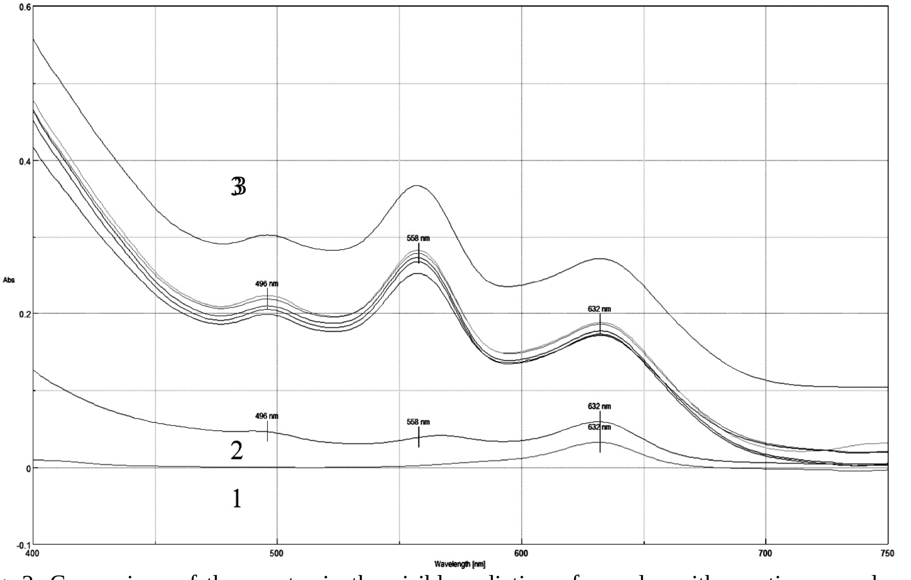

Fig. 2. Comparison of the spectra in the visible radiation of samples with sorption, samples of liquids prior to operation and samples of liquids regenerated using filtration methods (1 – the liquid before operation, 2 – the liquid after filtration and sorption with activated carbon CWZ14, 3 – the used liquid after filtration)

The spectra recorded help one to identify the colour of each sample, and thus enable the assessment of the sorptive capacity of individual materials. Spectrum 1, presented in Fig. 1, obtained for an antifreeze before its utilisation, has one signal associated with the absorption of radiation with the wavelength of 632 nm, characteristic for an orange colour. Absorption at this wavelength results in the formation of a green-blue colour. The spectrum obtained for an antifreeze in use, subjected to filtration, is presented in form of curve 3. There are three absorption bands, i.e. the signal at 496 nm that corresponds to absorption of the blue-green light (a red colour is observed), at 558 nm, which is equivalent to absorption of green radiation (a red-purple colouration is observed), and at 632 nm connected with the absorption of orange radiation (a blue-green colour can be observed). The presence of colouring compounds indicates the presence of complex chemical processes in which a structural material and an antifreeze take part. As a result, corrosive products containing metallic elements can be generated. The experiments the author conducted using sorptive materials indicate that it is possible to remove colouring agents, and the best results can be obtained when activated carbon CWZ 14 (spectrum 2) is used. Further spectral analyses employing ICP-MS techniques confirmed the removal of compounds containing metals, particularly copper and lead using sorptive materials. In Fig. 3, the author compares the intensity of a band characteristic for copper in a sample of antifreeze before sorption (curve 1) with a sample after sorption on the activated carbon (curve 3) and fly ash (curve 2).

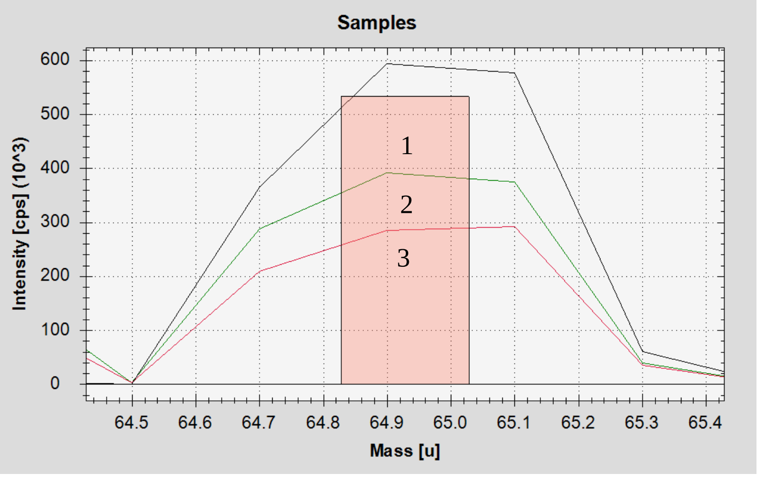

Fig. 3. The influence of the sorbent on the copper content in an antifreeze: 1) – the sample before sorption, 2) the CR+LP18.88 sample after sorption on volatile ash, 3) – the CR+WA14 sample after sorption on activated carbon

The presented results indicate that the removal of copper compounds is most effective when the CWZ-14 activated carbon is used. In the case of the removal of lead from water and glycol-based liquids by means of sorption, fly ashes are more effective, which directly stems from the analysis of the intensity of signals of masses obtained during ICP-MS tests (Fig. 4).

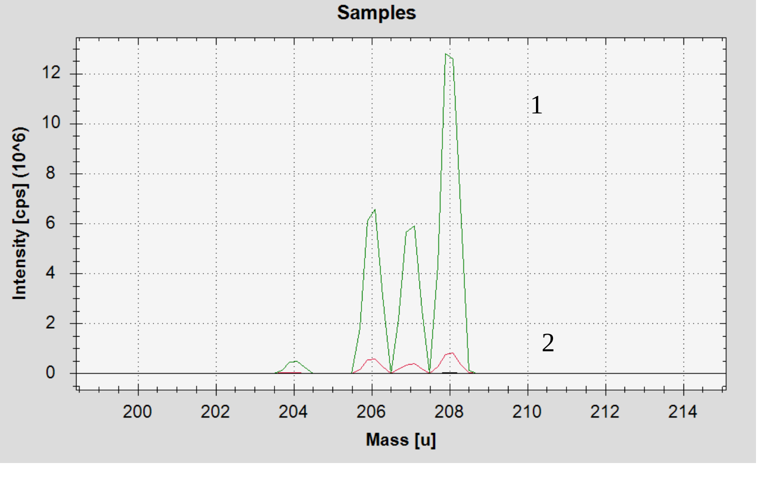

Fig. 4. Comparison of the intensity of the signals of lead present in the samples of a regenerated liquid: 1) activated carbon CWZ-14 (the CR+WA14 sample), 2) fly ash (the CR+LP18.88 sample), identified using the ICP-MS method

The results of the quantitative determination of copper and lead using the ICP-MS method, in samples before and after sorption on activate carbon CWZ-14, and fly ashes (18.88) are shown in Fig. 5.

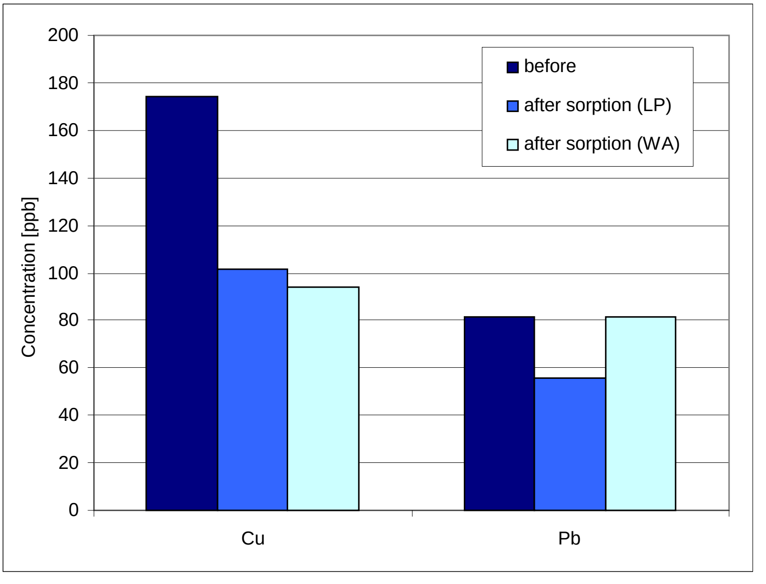

Fig. 5. Comparison of copper and lead content in an antifreeze before and after sorption

Based on spectral studies, the author confirmed the possibility to remove, by means of sorption, the aging colouring products and soluble copper and lead compounds from an antifreeze. However, it was necessary to check the impact of the sorption on basic performance parameters of water and glycol-based antifreezes determining the reliable functioning of the installation for heat exchange.

2.2. Investigation of operating properties of antifreezes

Experimental work helped the author to verify operating properties of antifreezes subjected to sorption. The key operating parameter that determines the possibility to utilise the liquid in a system for heat exchange is the flow temperature, which characterises the bottom line of a liquid flow, and at the same time describes the conditions of a reliable use of an installation in question. The results of the tests are presented in Fig. 6.

The results delineated above indicate that sorption of antifreezes, in majority of cases, does not influence their low temperature properties, which suggests that there is no loss of glycol during this process. Nonetheless, the use of the activated carbon CWZ-14 for the purification of antifreezes improves low temperature properties of these liquids, which can be observed as a reduction of the flow temperature. In this case, it is possible to adsorb low-molecule aging products from glycol without removing glycol molecules, which is confirmed by tests on the density of individual samples (Fig. 7).

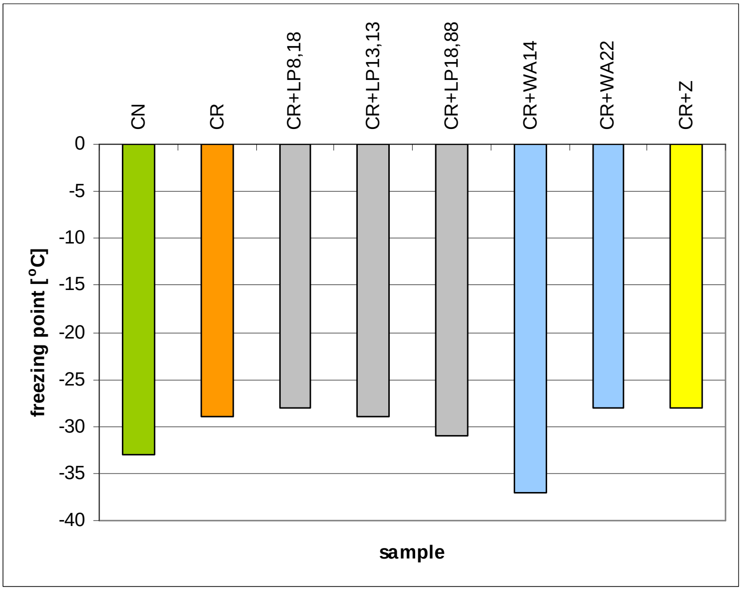

Fig. 6. The influence of sorption of an antifreeze on its freezing point

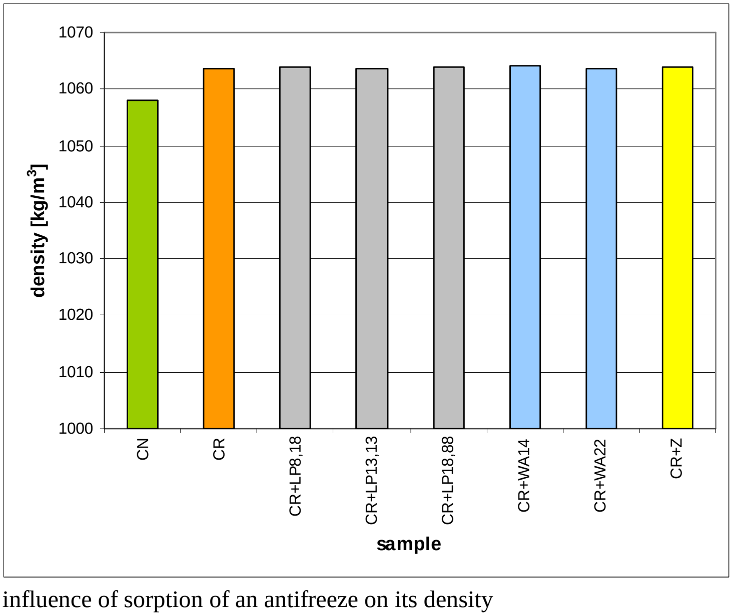

Fig. 7. The influence of sorption of an antifreeze on its density

The effectiveness of the removal of low-molecule acidic substances using selected sorbents was assessed based on the analysis of the results of tests on the alkaline reserve, which are presented in Fig. 8.

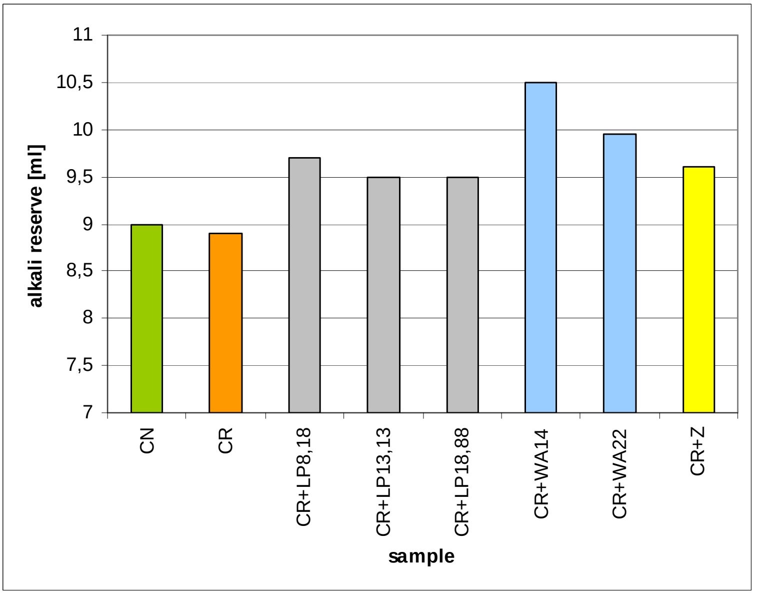

Fig. 8. The influence of sorption of an antifreeze on its alkaline reserve

The results of laboratory tests confirmed that sorption of antifreezes with all sorbents tested increases the alkaline reserve (Fig. 8), which is highly advantageous, since it reduces the corrosive impact of water and glycol-based antifreezes on structural elements of the installation. The best results were obtained when the activated carbon CWZ-14 was used as a sorbent. All the sorbents used increased the alkaline reserve to a value exceeding even the results obtained in tests on an unused antifreeze, which suggests that there is apparent penetration of the alkaline substances in these sorbents.

The author also verified the influence of sorption regeneration on the corrosive impact of a glycol-based liquid on selected metals. For that purpose, the mass loss of standardized plates immersed for 14 days in the test glycol liquid and thermostated at 88°C was determined. The results obtained before and after sorption, using selected sorbents, are shown in Fig. 9.

The tests results presented above show that the antifreeze has a corrosive effect, particularly on the binding material, i.e. the tin and lead alloy (the LC-30 alloy), and aluminium. The sorption regeneration conducted using activated carbon and fly ashes significantly reduced the corrosive impact of a glycol

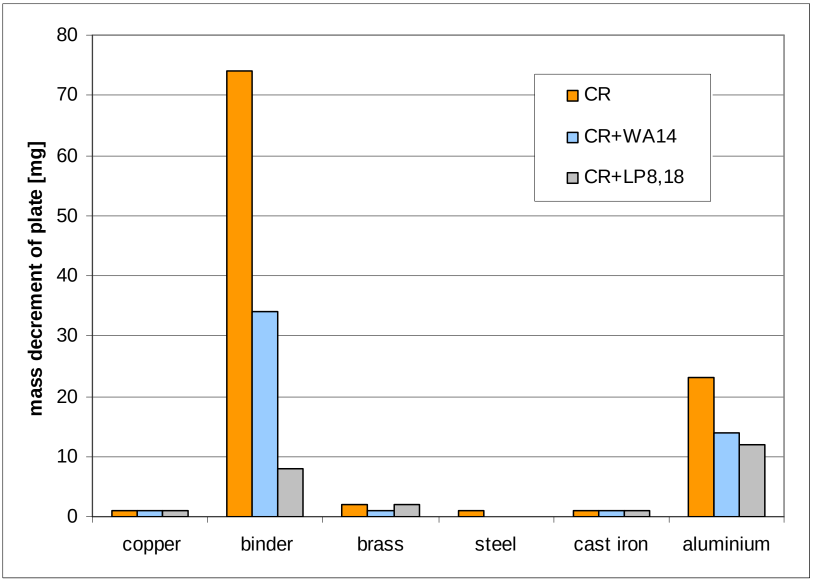

Fig. 9. The influence of sorptive regeneration on corrosive impact of an antifreeze on metals

liquid on the above-listed materials. It is also worth noting that fly ashes containing significant amounts of the unburned carbon, constituting onerous waste from power plants, can be an excellent absorbent material enabling the reduction of the corrosive impact of an antifreeze. In the case of a liquid not subjected to regeneration, this impact can be reduced by over 80%, while in the case of aluminium, this impact can be reduced by nearly 50%. The activated carbon CWZ-14 is also an effective absorbent material, and its application can reduce the corrosive impact of a regenerated liquid by ca. 50% with reference to the corrosive impact of a non-regenerated liquid.

Conclusions

The analysis of test results indicates that sorption has no effect on the density of the regenerated antifreeze. However, it does enable the removal of colouring substances and chemical compounds containing heavy metals. The author also noticed that, in some cases, an improvement in low temperature properties (described with a flow temperature) is observed for sorption treated samples, compared to samples subjected to mechanical filtration only. Such an effect is present in the case of samples subjected to sorption using activated carbon type CWZ-14. Moreover, sorption has a significant impact on the increase of alkaline reserve of the processed samples, which in turn reduces the corrosive impact of an antifreeze, particularly on aluminium and a bonding material (i.e. the tin or lead alloy). This not only indicates the removal of acidic substances from regenerated samples, but also proves that alkaline substances present in a sorbent used are dissolved by the treated liquid.

The analysis of the results of tests on physicochemical properties of a regenerated glycol liquid indicates that it is possible to re-use it in heat exchange installations. The most effective among the tested sorbents is activated carbon CWZ-14, as well as fly ash with a high content of unburned carbon. Therefore, the author also confirmed the possibility of industrial application of appropriate fly ashes, constituting waste from the power industry, otherwise impossible to be used in typical applications, i.e. as an additive to building materials.

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Scientific work executed within “Innovative Systems of Technical Support for Sustainable Development of Economy” Strategic Programme within Innovative Economy Operational Programme.

Ocena przydatności sorbentów nieorganicznych w procesach regeneracji wodno-glikolowych przemysłowych cieczy niskokrzepnących

Słowa kluczowe

Ciecze niskokrzepnące, starzenie eksploatacyjne, regeneracja sorpcyjna, właściwości eksploatacyjne, wymienniki ciepła.

Streszczenie

W artykule przedstawiono wyniki badań w zakresie sorpcyjnej regeneracji wodno-glikolowej cieczy niskokrzepnącej, eksploatowanej w przemysłowej instalacji wymiany ciepła. Jako sorbenty stosowano węgle aktywne, zeolity oraz lotne popioły o wysokich zawartościach niewypalonego węgla, stanowiące odpad powstający w elektrowni konwencjonalnej. Przeprowadzono badania za pomocą spektrofotometru UV-Vis oraz spektrometru z plazmą sprzężoną indukcyjnie wyposażonego w detektor mas (ICP-MS). Zbadano także właściwości fizykochemiczne cieczy regenerowanej, tj.: gęstość, rezerwę alkaliczną, temperaturę płynięcia oraz działanie korodujące na metale i wyniki porównano z parametrami cieczy przed regeneracją oraz cieczy nieeksploatowanej. Potwierdzono możliwość poprawy parametrów fizykochemicznych cieczy niskokrzepnącej, głównie rezerwy alkalicznej oraz usuwanie rozpuszczalnych związków zawierających miedź i ołów oraz związków barwnych poprzez obróbkę sorpcyjną. Stwierdzono także ograniczenie korozyjnego działania na metale cieczy zregenerowanej w porównaniu z preparatem niepoddanym sorpcji. Najefektywniejszymi sorbentami był węgiel aktywny typu CWZ-14 oraz lotne popioły o zawartości węgla powyżej 8% masowych.