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EXAMINATION OF BIOGAS HYDROGEN SULPHIDE SORPTION ON A LAYER OF ACTIVATED BOG ORE

The efficiency of hydrogen sulphide removal from biogas using bog ore-based desulphurizing pulp is investigated. Measurements were carried out on quarterly basis over a five-year period in one of Polish municipal sewage treatment plants. Measurement results are presented as a function of H₂S removal efficiency drop over time, with the resulting times of desulphurizing layer breakthrough compared with theoretical calculations. Sorption capacity, per unit consumption, and relative cost of the sorbent were estimated, which allows the results to be generalized and applied in comparable treatment plants.

1. INTRODUCTION

The development of renewable energy sources, such as biogas, is one of the priorities of national economy. This obligation results not only from the adoption of EU standards, but also from ecological, economic and political considerations. One of the most widely used and developed sources of biogas in Poland is the process of sewage sludge fermentation. Since 2002, the Institute of Environmental Engineering at Wrocław University of Technology has conducted quarterly measurements of physical and chemical parameters of biogas at one of Polish mechanical and biological municipal waste treatment plants with the output of 80000 m³/d. Biogas produced as a result of anaerobic fermentation of sludge is dehydrated, treated in desulphurizers and adsorbers, filtered and, ultimately, used as fuel in combined heat and power (CHT) aggregates and boiler rooms. The resulting energy and heat are utilized in the plant, with subsequent annual cost reduction (energy saving and resale of Certificates of Origin) of nearly 600 thousand euros.

Biogas samples collected at eight points of the transmission/treatment system are examined to establish the following indexes and parameters:

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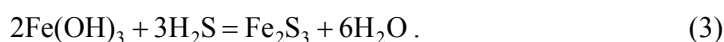
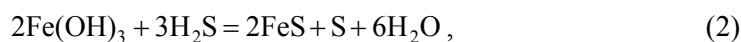
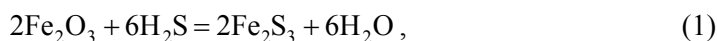
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- basic chemical composition, including CH₄, CO₂, N₂, O₂ and H₂ content;
- energy parameters, i.e. heat of combustion, calorific value and the Wobbe index;
- density, humidity, pressure and temperature;
- concentration of H₂S, NH₃ and total sulphur, chlorine, fluorine, silicon, oils and dust.

This paper is based on the concentration measurements of H₂S collected both upstream and downstream in the desulphurizers. Manufacturer's requirements limit the H₂S upstream content of biogas in exhaust catalyst generators to 1150 mg H₂S/10 kWh (corresponding roughly to 700 mg/m³), and the upstream content in activated carbon adsorbers (figure 1) – to 200 mg/m³ (the index *n* corresponds to standard conditions, i.e. 273 K, 1013 hPa and dry gas).

Technical biogas desulphurisation utilizes different methods, all of them well-documented in professional literature. The common feature of those methods is the preservation of a basic biogas component, i.e. methane. Removal of H₂S from biogas may be based on the following processes: physical absorption [1]–[3], absorption with chemical and/or catalytic reactions [2], [4], [5], adsorption [6]–[10], adsorption with chemical and/or catalytic reactions [11]–[17], microbiologic reactions [18]–[26].

Two-stage sludge fermentation is another common method allowing the H₂S content in biogas to be decreased. In the world industry practice, there are used nearly several dozen alternative methods, depending on technological requirements and financial resources. Because of its low price, the most widely used method is sorption with a chemical reaction with iron compounds (Fe⁺³), easily accessible in Poland in the form of bog ore. The process may run as follows:



The precondition of the process is the presence of iron in the form of Fe₂O₃·H₂O hydrate or Fe(OH)₃ hydroxide. The reaction mechanism is influenced by: temperature, humidity and pH of the reaction environment. Reaction (2) takes place in alkaline environment, while reaction (3) – in neutral. The hydrate variants of αFe₂O₃·H₂O and γFe₂O₃·H₂O react easily with hydrogen sulphide, which produces sulphides easily oxidizable to active compound of iron oxide (III). The process is most efficiently run at temperatures of ca. 310 K in alkaline environment.

2. INSTALLATION AND DESULPHURIZING PULP UNDER STUDY

Waste sludge from primary sedimentation and secondary treatment tanks (figure 1), after dehydration and thickening, are transported to two closed fermentation

chambers (1) with capacity of 6500 m³ each. Biogas produced in the chambers, at the rate of 200–250 m³/h, is treated in a desulphurizer (2) filled with four layers of the desulphurizing agent under study of 0.225 m depth each and of a total volume $V = 3.4$ m³. The desulphurized biogas is stored in a low-pressure, double-lined tank (3), and – via a measurement and distribution node (4) – directed to a boiler room (11) and generators (7) of a nominal electric power of 600 kW each. In emergency, biogas surplus is burned in gas flare (12). The biogas directed to generators is additionally treated in an adsorber (5) filled with activated carbon and passed through a fibrous filter (6). The exhaust gases, cooled via a heat exchange device (8), are passed through a catalytic converter (9) and expelled through chimneys (10).

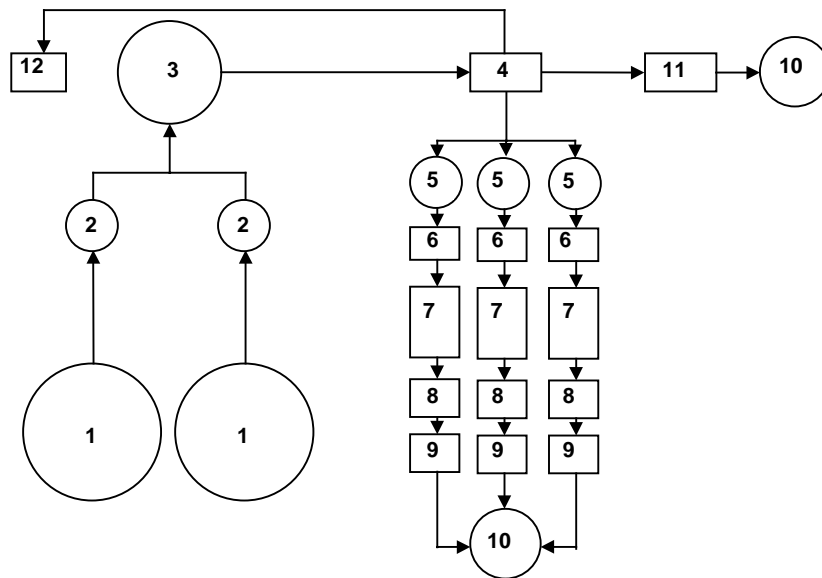


Fig. 1. Diagram of production, storage, transmission, treatment and utilisation of biogas:
 1 – fermentation chamber, 2 – desulphurizer, 3 – tank, 4 – measurement/distribution node,
 5 – adsorber, 6 – filter, 7 – generator, 8 – heat exchanger, 9 – catalytic converter,
 10 – chimney, 11 – boiler plant, 12 – gas flare

The desulphurizing pulp under study was prepared on the basis of bog ore from the Polish deposits in Strzyżów near Kalisz, in accordance with specifications developed at the Faculty of Chemistry, Assembly of Chemistry and Fuel Technology of Wrocław University of Technology. Raw bog ore was supplemented with alkaline activators and aerating additives. Average pulp composition is shown in table 1.

Table 1

Averaged results of desulphurizing pulp laboratory analyses (years 2002–2007)

| Parameter | Unit | Value |
|--|-------------------|-------|
| pH of water extract | – | 9.1 |
| Humidity (<i>h</i>) | % | 49.9 |
| Concentration of aerating additives | % d.m. | 9.1 |
| Concentration of alkaline activators | % d.m. | 3.4 |
| Concentration of Fe ⁺³ (<i>b</i>) | % d.m. | 22.1 |
| Sorptive capacity of S | % S/kg d.m. | 18.8 |
| Density of humid pulp (ρ) | kg/m ³ | 941 |

3. MEASUREMENT AND ANALYTIC METHODS

H₂S was absorbed in zinc acetate solution and measured spectrophotometrically. The absorbed H₂S was treated with *N,N*-dimethyl-*p*-phenyldiamine in the presence of iron chloride (III). The reaction product was methylene blue – a basis for quantification. Gas pressure at measurement points was high enough to force the flow through bubbling gas washers and gas-meters, allowing elimination of electric aspirators or pumps.

Due to field character of the research and assumed cyclic timetable, the measurements were conducted under current on-site conditions of the installation, environment and actual sorbent saturation.

The measurement results were grouped into 8 measurement series, starting from the date of desulphurizing pulp replacement (except for series 1 and 2, lacking their corresponding data). Each series, after averaging the results for both desulphurizers, were plotted as a function of H₂S removal efficiency change with time. The points from each series were plotted against a trend plot averaged from all measurements, representing the drop in desulphurizing efficiency with time.

4. RESULTS AND DISCUSSION

Based on the analysis of a trend plot (figure 2), obtained from measurements (table 2), an average drop of H₂S removal efficiency was calculated at a value of 0.41%/d. This value was used to calculate an average time of deposit depletion (τ_w):

$$\tau_w = \frac{100\%}{0.41\%/d} = 244 d, \quad (4)$$

which was then compared with theoretically calculated depletion time (τ_o):

$$\tau_0 = \frac{m_{\text{H}_2\text{S}}}{\dot{m}_{\text{H}_2\text{S}}} = \frac{\rho \cdot V \cdot \frac{h}{100} \cdot \frac{b}{100} \cdot M_{\text{H}_2\text{S}}}{8 \cdot M_{\text{Fe}} \cdot L \cdot C \cdot \frac{\eta_a}{100} \cdot 10^{-6}} = 472 \text{ d}, \quad (5)$$

where:

$m_{\text{H}_2\text{S}}$ – stoichiometric quantity of converted H_2S mass; kg,

$\dot{m}_{\text{H}_2\text{S}}$ – average mass flow of removed H_2S ; kg/h,

M – respective mole mass; kg/kmol,

C – average H_2S concentration at desulphurizer inlet (table 2); mg/m_n^3 ,

V – fixed-bed volume; m^3 ,

η_a – average H_2S removal efficiency (table 2); %,

ρ, h, b – as in table 1.

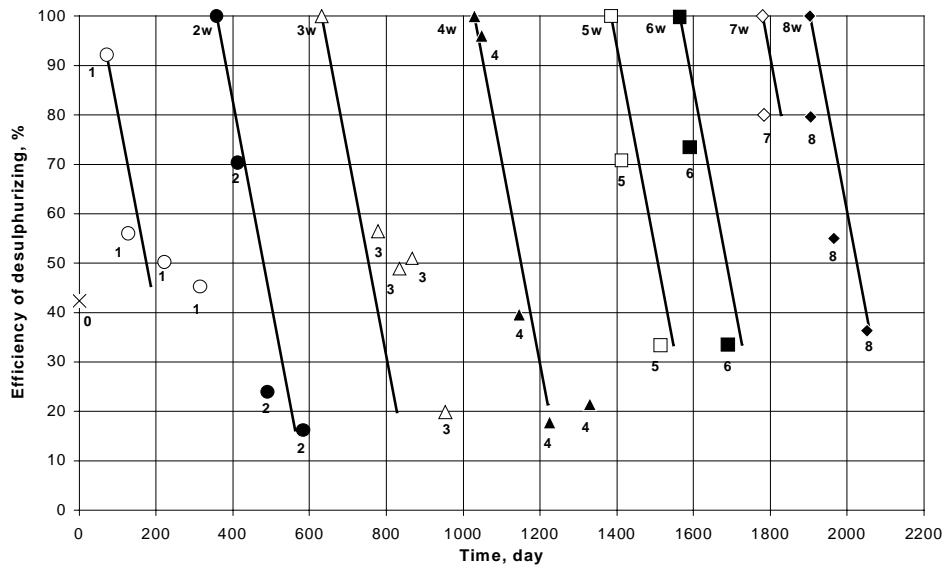


Fig. 2. Changes in H_2S removal efficiency in desulphurizers:
w – desulphurizing pulp replacement, 1 – No. of measuring series

Average biogas flow in standard conditions ($L = 221 \text{ m}_n^3/\text{h}$) was calculated from a known average electric power of generators during measurement (430 kW) and a power-to-flow formula (1.9475) based on our own research. Flow examinations were carried out for three power values (600 kW, 450 kW, 300 kW) and the CH_4 content in biogas analogous to its average content in all measuring series (65%).

Table 2

Overview of measurement results

| Measurement series | Date of investigation | Date of sorbent replacement | Desulphurizer 1 | | | Desulphurizer 2 | | |
|--------------------|-----------------------|-----------------------------|---|--------|------------|---|--------|------------|
| | | | H ₂ S concentration (mg/m ³) | | η (%) | H ₂ S concentration (mg/m ³) | | η (%) |
| | | | Inlet | Outlet | | Inlet | Outlet | |
| 0 | 01.08.2002 | lack of data | 319 | 212 | 33.5 | 332 | 162 | 51.2 |
| 1 | 11.10.2002 | lack of data | 258 | 28 | 89.1 | 298 | 14 | 95.3 |
| 1 | 06.12.2002 | | 364 | 127 | 65.1 | 273 | 145 | 46.9 |
| 1 | 10.03.2003 | | 261 | 87 | 66.7 | 222 | 147 | 33.8 |
| 1 | 11.06.2003 | | 286 | 180 | 37.1 | 312 | 145 | 53.5 |
| 2 | 17.09.2003 | 23.07.2003 | 206 | 71 | 65.5 | 242 | 60 | 75.2 |
| 2 | 03.12.2003 | | 210 | 173 | 17.6 | 201 | 140 | 30.3 |
| 2 | 05.03.2004 | | 126 | 103 | 18.3 | 150 | 129 | 14.0 |
| 3 | 16.09.2004 | 18.04.2004 | 276 | 128 | 53.6 | 334 | 136 | 59.3 |
| 3 | 10.11.2004 | | 201 | 96 | 52.2 | 189 | 103 | 45.5 |
| 3 | 14.12.2004 | | 120 | 72 | 40.0 | 118 | 45 | 61.9 |
| 3 | 10.03.2005 | | 105 | 102 | 2.9 | 128 | 81 | 36.7 |
| 4 | 13.06.2005 | 2.06.2005 | 119 | 5 | 95.8 | 105 | 4 | 96.2 |
| 4 | 19.09.2005 | | 179 | 100 | 44.1 | 160 | 104 | 35.0 |
| 4 | 08.12.2005 | | 275 | 239 | 13.1 | 323 | 251 | 22.3 |
| 4 | 15.03.2006 | | 212 | 157 | 25.9 | 223 | 185 | 17.0 |
| 5 | 12.06.2006 | 13.05.2006 | 89 | 32 | 64.0 | 67 | 15 | 77.6 |
| 5 | 22.09.2006 | | 52 | 34 | 34.6 | 56 | 38 | 32.1 |
| 6 | 06.12.2006 | 9.11.2006 | 85 | 19 | 77.6 | 75 | 23 | 69.3 |
| 6 | 07.03.2007 | | 109 | 73 | 33.0 | 100 | 66 | 34.0 |
| 7 | 19.06.2007 | 13.06.2007 | 84 | 17 | 79.8 | 800 | 16 | 80.0 |
| 8 | 18.10.2007 | 16.10.2007 | 165 | 23 | 86.1 | 148 | 40 | 73.0 |
| 8 | 17.12.2007 | | 136 | 62 | 54.4 | 126 | 56 | 55.6 |
| 8 | 12.03.2008 | | 64 | 37 | 42.2 | 69 | 48 | 30.4 |
| average | | | 179 | 91 | 50 | 180 | 90 | 51 |

η is the efficiency of H₂S removal.

Based on experimentally calculated average time of sorbent depletion and load of removed H₂S, actual value of desulphurizing pulp sorption ability (Q) was calculated:

$$Q = \frac{L \cdot C \cdot \frac{\eta_a}{100} \cdot \frac{32}{34} \cdot 10^{-6} \cdot 8760}{\frac{365}{\tau_w} \cdot V \cdot \frac{h}{100} \cdot \rho} = 0.068 \text{ kg S/kg d.m.} \quad (6)$$

Assuming a minimum desulphurizing efficiency of 25%, a maximum work time of the deposit (τ_p) may be calculated:

$$\tau_p = \frac{100\% - 25\%}{0.41\%/d} = 183 \text{ d} . \quad (7)$$

If the annual desulphurizing pulp demand $\left(V_{\text{ods}} = 2 \cdot \frac{365}{\tau_p} \cdot V = 13.6 \text{ m}^3 \right)$ is known, it is possible to calculate the pulp consumption index per 1000 m_n^3 of the biogas fed:

$$W_{\text{ods}} = \frac{V_{\text{ods}} \cdot 1000}{8760 \cdot 2 \cdot L} = \frac{13.6 \cdot 1000}{8760 \cdot 2 \cdot 221} = 0.0035 \text{ m}^3 / 1000 \text{ m}_n^3 \quad (8)$$

as well as the exploitation cost per unit required for the purchase of desulphurizing pulp (per each 1000 m_n^3 of biogas):

$$K = 0.0035 \text{ m}^3 / 1000 \text{ m}_n^3 \cdot 730 \text{ euros/m}^3 = 2.6 \text{ euros} / 1000 \text{ m}_n^3 . \quad (9)$$

5. CONCLUSIONS

- A long-standing examination of H_2S sorption from biogas at a selected site allowed one to calculate a trend plot representing a drop in the removal efficiency of the sorbent under study as a function of time. The resulting function can be used to predict the time of replacing the sorbent under study.

- Sorbability of the agent under study, produced on the basis of bog ore and alkaline activators, calculated for the average, all-season operating conditions of the selected treatment facility, amounts to 36% of sorbability calculated in the laboratory. This may be attributed to practical difficulties in satisfying the optimal parameters of desulphurizers in field application, such as pH, temperature and humidity.

- The field-calculated time of sorbent depletion amounts to 52% of the time calculated from the stoichiometry of the chemical reactions involved (disregarding the role of activators).

- In the facility under study, desulphurisation of biogas using the analysed sorbent allows one to obtain H_2S concentration well below the technically required value of 200 mg/m_n^3 .

- The experimentally calculated index of desulphurizing pulp consumption amounts to 0.0035 $\text{m}^3 / 1000 \text{ m}_n^3$ of biogas (i.e. ca. 3.3 $\text{kg} / 1000 \text{ m}_n^3$), with purchase cost per unit at ca. 2.6 euros/1000 m_n^3 .

REFERENCES

- [1] MOHR V.H., *Acid and Sour Gas Treating Processes*, Chem. Eng. Progr., 1984, 10, 27–34.
- [2] MOLENDĄ J., *Nowe rozwiązania technologiczne w schematach odsiarczania gazów ziemnych*, GWiTS, 2000, 6, 211–219.
- [3] CZEMPLIK M., *Odsiarczanie biogazu – dylematy projektanta*, Ekotechnika, 1997, 3, 24–25.
- [4] ERMICH S., PRUSZYŃSKA E., *Biosulfex – nowa metoda odsiarczania biogazu*, GWiTS, 2000, 1, 3–5.
- [5] MANSFIELD L.A., MELNYK P.B., RICHARDSON G.C., *Selection and full scale use of chelated iron absorbent for odor control*, Water Environ. Res., 1992, 2, 120–127.
- [6] BAGREEV A., ADIB F., BANDOSZ T.J., *pH of activated carbon surface as an indication of its suitability for H₂S removal from moist air streams*, Carbon, 2001, 39, 1897–1905.
- [7] ADIB F., BAGREEV A., BANDOSZ T.J., *Analysis of the relationship between H₂S removal capacity and surface properties of unimpregnated activated carbons*, Environ. Sci. Technol., 2000, 34, 686–692.
- [8] BAGREEV A., MENENDEZ A., DUKANO I., TARASENKO Y., BANDOSZ T.J., *Bituminous coal based activated carbons modified with nitrogen as adsorbents of hydrogen sulfide*, Carbon, 2004, 42, 469–476.
- [9] CRESPO D., QI G., WANG Y., YANG F.H., YANG R.T., *Superior sorbent for natural gas desulphurization*, Ind. Eng. Chem. Res., 2008, 47, 1238–1244.
- [10] GUAO J., LUO Y., LUA A.C., CHI R., CHEN Y., BAO X., XIANG S., *Adsorption of hydrogen sulfide by activated carbons derived from oil-palm Stell*, Carbon, 2007, 45, 330–336.
- [11] BANDOSZ T.J., *On the adsorption/oxidation of hydrogen sulfide on activated carbons at ambient temperature*, J. Colloid Interface Sci., 2002, 246, 1–20.
- [12] XIAO Y., WANG S., WU D., YOUAN Q., *Catalytic oxidation of hydrogen sulfide on unmodified and impregnated activated carbon*, Sep. Purif. Technol., 2008, 59, 326–332.
- [13] TURK A., SAKALIIS E., LESSUCK J., KARAMITSOS H., RAGO O., *Ammonia injection enhances capacity of activated carbon for hydrogen sulfide and methyl mercaptan*, Environ. Sci. Technol., 1989, 23, 1242–1245.
- [14] YAN R., LIANG D.T., TSEN L., TAY J.H., *Kinetics and mechanisms of H₂S adsorption by alkaline activated carbon*, Environ. Sci. Technol., 2002, 36, 4460–4466.
- [15] TSAI J., JENG F., CHIANG H.-L., *Removal of H₂S from exhaust gas by use of alkaline activated carbon*, Adsorption, 2001, 7, 357–366.
- [16] MASUDA J., FUKUYAMA J., FUJII S., *Ozone injection into an activated carbon bed to remove hydrogen sulfide in the presence of concurrent substances*, J. Air & Waste Manage. Assoc., 2001, 51, 750–755.
- [17] MEEYOO V., TRIMM D.L., *Adsorption-reaction process for removal of hydrogen sulfide from gas streams*, J. Chem. Tech. Biotechnol., 1997, 68, 411–416.
- [18] DUAN H., KOE L.C.C., YAN R., *Treatment of H₂S using a horizontal biotrickling filter based on biological activated carbon: reactor setup and performance evaluation*, Appl. Microbiol. Biotechnol., 2005, 67, 143–149.
- [19] DUAN H., YAN R., KOE L.C.C., WANG X., *Combined effect of adsorption and biodegradation of biological activated carbon on H₂S biotrickling filtration*, Chemosphere, 2007, 66, 1684–1691.
- [20] BALL A.S., NEDWELL D.B., PERKINS R.G., *Oxidation of hydrogen sulfide in sour gas by Chlorobium limicola*, Enzyme Microb. Technol., 2007, 41, 702–705.
- [21] LEE E.Y., LEE N.Y., CHO K., RYU H.W., *Removal of hydrogen sulfide by sulfate-resistant Acidithiobacillus thiooxidans AZ11*, J. Biosci. Bioeng., 2006, 101, 309–314.
- [22] GADRE R.V., *Removal of hydrogen sulfide from biogas by chemoautotrophic fixed-film bioreactor*, Biotechnol. Bioeng., 1989, 34, 410–414.
- [23] OYARZUN P., ARANCIBIA F., CANALES C., AROCA G.E., *Biofiltration of high concentration of hydrogen sulfide using Thiobacillus thioparus*, Process Biochem., 2003, 39, 165–170.

- [24] JENSEN A.B., WEBB C., *Treatment of hydrogen sulfide-containing gases: A review of microbiological alternatives*, Enzyme Microb. Technol., 1995, 17, 2–10.
- [25] POTIVICHAYANON S., POKETHITTIYOOK P., KRUAATCHUE M., *Hydrogen sulfide removal by a novel fixed-film bioscrubber system*, Process Biochem., 2006, 41, 708–715.
- [26] YANG Y., ALLEN E.R., *Biofiltration control of hydrogen sulfide*. 1. *Design and operational parameters*, J. Air & Waste Manage. Assoc., 1994. 44, 863–868.

BADANIA SORPCJI SIARKOWODORU ZAWARTEGO W BIOGAZIE NA UAKTYWNIONEJ RUDZIE DARNIOWEJ

Przedstawiono wyniki badań nad skutecznością usuwania siarkowodoru z biogazu za pomocą masy odsiarczającej utworzonej na bazie rudy darniowej. Pomiarów wykonywano co kwartał, przez pięć lat, w jednej z krajowych oczyszczalni ścieków miejskich. Wyniki pomiarów opracowano w postaci zależności zmniejszania się skuteczności usuwania H_2S od czasu, a uzyskane czasy „przebiecia” złoża porównano z czasami obliczonymi teoretycznie. Określono chłonność, jednostkowe zużycie oraz oszacowano względne koszty sorbentu, co pozwoliło uogólnić wyniki badań i wykorzystać je w podobnych obiektach.