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TIME CHANGEABILITY MODEL OF THE BOG ORE SORPTION ABILITY

MODEL CZASOWEJ ZMIENNOŚCI ZDOLNOŚCI SORPCYJNEJ RUDY DARNIOWEJ

Abstract: Basing on long-standing cyclic measurements of sludge-originated biogas composition and considering statistical analysis of their results, a regression model describing time variation of biogas desulfurization using bog iron ore has been developed. The model was verified by theoretical calculations and results from laboratory examinations of the sorbent. It was also used to estimate the depletion time and sorption capacity of the bed and to determine the demand index for bog ore.

Keywords: sewage sludge, fermentation, biogas, desulphurization, statistical analysis, forecasting

Introduction

Development of renewable energy sources is one of the priorities of European Union's policy. According to the Development Strategy of Renewable Energy Sources approved by Polish Parliament in 2001, Poland is planning, as a part of this policy and commitments undertaken, to double the share of renewable energy in the total balance of primary energy carriers (up to 15%) by 2020. According to this Strategy, the biomass including also biogas, is to be the main renewable energy source. This is confirmed by the project "National Executive Plan for Energy from Renewable Sources" prepared by the Ministry of Economy in 2010 which represents the commitments resulting from the Directive 2009/28/EU of the European Parliament and the Council on the promotion of the use of energy from renewable source. Pursuant to this plan, the national output of biogas in 2012 was 7033 TJ, 47% of which referred to biogas generated from sludge and 32% - from dumping site biogas. At the end of 2013, there were 231 biogas plants in Poland (160 MW_e), out of which just 17%represented agricultural biogas units. It can be expected that their share would be essentially higher in forthcoming years. According to Poland's Power Engineering Policy by 2030 as prepared by the Ministry of Economy in 2009, wind power engineering, production of biogas and solid biomass, and also transport bio-fuels would be of decisive importance in

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reaching the aforementioned 15% target, and according to above "National Executive Plan ...", expectations are that, on an average, one agricultural biogas plant will be constructed in each commune by 2020.

Having regard to the boom forecasted for biogas plants [1-3], it would be necessary to develop biogas treatment methods, especially in the context of its industrial combustion. Removal of sulphur hydrogen, which creates threat for instrumentation and environment, is among one of the most important stages in biogas treatment process [4]. Due to availability of the sorbent and low related capital and operating costs, bog ore, the mineral including iron compounds reacting with H_2S , is commonly used for this purpose in Poland. However a barrier for its further effective use may be the lack of experimental data about its sorption capacity, mechanisms of sorption and the possibilities of its intensification.

The mathematical model of time variability of biogas desulfurization efficiency using bog ore was developed basing on long-standing (2003-2009), quarterly examinations of biogas generated from sludge in Wroclaw Sewage Treatment Plant [5]. It was then used to calculate the bed sorption capacity and to determine the sorbent demand index per 1000 m³ of biogas. The results from model calculations were compared with sorption capacity calculated theoretically and with the results of laboratory examinations.

This paper is continuation of the previous examinations [6]. Information about analytical methods is given in items [5-8] while that of generation and treatment of biogas under investigation - in [5].

Biogas desulphurization using bog ore

Biogas can be cleared out of H_2S through the following processes: physical absorption [9], absorption including chemical and/or catalytic reaction [10], adsorption [11-15], adsorption including chemical and/or catalytic reaction [16-22], and microbiological reactions [23-31]. Absorption including catalytic reaction using Fe⁺³ iron compounds [32], which are easily and at low cost available in Poland, *ie* the bog ore, is the most popular method presented below. As regard geological aspect, the bog ore is a low-depth deposited Quaternary mineral formerly used in iron metallurgy and building engineering. Most often it is qualified as limonite (fine-grained or cryptocrystalline sedimentary rock being generally a mixture of iron oxides and hydroxides). It comes into existence as a result of biochemical and oxidation processes over areas of waterlogged meadows, peatbogs and marshy grounds (also called "meadow ore"). There are favourable conditions for its formation in our climatic zone, especially on the area of Polish Lowland [33]. The ore is deposited at depths up to 1 m which directly affects its low cost of winning. Pursuant to the Ordinance of the Minister of Environmental Protection of 18 December 2001 on the criteria of balancing the mineral deposits (Journal of Laws 2001.153.1774), "fine" and "lumped" forms are distinguished. An interesting feature of bog ore is its natural renovating capability following it is worked out, it grows again in a dozen or so years and at the most in several dozen years.

Chemical constitution of the ore is dominated by Fe_2O_3 (from 47 to 58% in fine forms and from 37 to 71% in lumped forms) and SiO_2 (11-15% and 37-69%, respectively). There are also P_2O_5 and MnO_2 from several to a dozen or so percent. Detailed chemical analysis and variability of ore forms are shown in [33]. As concerns the mineral aspects, three groups of iron phase joints are distinguished: ferrihydride ($Fe_5O_6(OH)_3$ ·3H₂O), goethite (α -FeOOH) and lepidocrocite (γ -FeOOH). Apart from oxide minerals, iron is also present in carbonates found in bog ores, *ie* siderite (FeCO₃), oligonite ((Fe,Mn)CO₃) and phosphates - *eg* vivianite (Fe₃(PO₄)₂·8H₂O). The ore includes also silty minerals (kaolinite, illite, smectice). Besides the crystalline components, bog ores contain amorphous, also organic, substances [34]. The key feature of a sorbent, which represents its adsorption properties, is the value of specific surface (BET). It varies, among different ore forms, from *ca* 30 to over 240 m²/g [35]. The radii of micropores are from 5 to do 25 Å, the capacity of cation exchange - from several to 50 mval/100 g and the capacity of anion exchange - up to several mval/100 g [33]. Fine ores have larger specific surfaces, higher number of pores and larger capacities of ion exchanges. The content of iron oxides and organic substance in the ores is of the highest importance for its sorption properties. By fixing to surface of ore mineral components (mainly iron oxide-hydroxides and hydroxides), humus substances block the sorbent pores [36]. There are no bibliography references with simple relationships between composition of bog ores and their sorption properties.

For the bog ore could be the H_2S sorbent, it shall be made free of minus 200 µm grain size fraction, organic substances and carbonate minerals. Activation of the ore consists in calcining at 673 K [36], fluffing (*eg* by adding sawdust) and alkalizing with calcium hydroxide, sodium hydroxide or sodium carbonate (hydroxides bond with CO₂ to carbonates which are also reacting with H_2S). The aforementioned methods of chemical and physical activation allow to enlarge the specific surface and porosity, to improve alkaline-acid properties, hydrophilicity or hydrophobicity and also catalyst properties [36].

Mechanism of biogas desulfurization using bog ore is strongly dependent on pH value. In neutral and alkaline environment (where NaOH is the activator), the process can run according to the following reactions:

$$2Fe(OH)_3 + 3H_2S \rightarrow Fe_2S_3 + 6H_2O \tag{1}$$

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \tag{2}$$

$$2NaOH + H_2S \rightarrow Na_2SO_3 + 2H_2O$$
(3)

and accordingly, in acid environment:

$$2Fe(OH)_3 + 3H_2S \rightarrow 2FeS + S + 6H_2O \tag{4}$$

$$2\text{FeOOH} + 3\text{H}_2\text{S} \rightarrow 2\text{FeS} + \text{S} + 4\text{H}_2\text{O}$$
(5)

Alkaline medium is more favourable as it generates Fe_2S_3 which faster reacts with oxygen. This facilitates regeneration consisting in oxidizing ferrous sulphide(III) back to the active form of ferrous oxide(III). In acid environment, the free sulphur coming out in a process, blocks the pores and faster deactivates active iron compounds. The process goes the best at about 310 K. Bog ore sorbent should have humidity of about 50%, $Fe_2O_3 \cdot H_2O$ content above 60% of dry mass and pH value of water extract above 8. In theory, 1 kg of Fe_2O_3 may bind 0.64 kg H_2S . In practice, when gas mixture is free of oxygen, the saturation of 0.3-0.5 kg H_2S/kg of dry ferrous oxide(III) is attained.

Material and methods

Two parallel cylindrical desulfurization grid-type units with four filtration baskets 2.2 m in diameter and bed layer height 0.20-0.25 m are used for biogas desulfurization at Wroclaw Sewage Treatment Plant (WSTP). The units are filled with bog ore from Strzyzow

deposits near Kalisz, prepared according to the recipe of the Institute of Chemistry, Petroleum and Coal Technologies at Wroclaw University of Technology (Table 1). Raw ore was modified by addition of alkaline activators (NaOH, Na₂CO₃) and fluffing agents in form of sawdust.

Devery	Unit	Value			
Farameter	Umt	Raw bog ore	Activated bog ore		
pH	-	5.28	9.18		
Humidity (w)	[%]	38.46	49.63		
Total Fe content	[% d.m.]	25.39	26.23		
Sawdust content	[% d.m.]	-	9.31		
Alkaline activator (A) content	[% d.m.]	-	3.38		
Fe^{+3} content - as Fe_2O_3 (B)	[% d.m.]	24.08	22.91		
Residuum unresolved in HCl	[% d.m.]	32.10	37.32		
Calcination losses at 1123 K	[% d.m.]	39.17	41.25		
Bog ore sorptive capacity	[% S/kg d.m.]	-	≥ 18.78		

Average results of laboratorial bog ore investigations (2003-2009)

d.m. - dry matter, S - sulphur

Statistical analyze

The model was developed on the basis of testing the biogas desulfurization efficiency (η) and dates of bed replacement (Table 2). Examinations were grouped in 10 measurement series commencing each time from the date of bed replacement. In calculations, averaged values from both desulfurization units were used.

Results of biogas desulphurization tests

Table 2

			Desulphurizer 1			Desulphurizer 2		
Number of series /colour of point - Fig. 2	Date Date of test of bed change	Date of bed change	H ₂ S concentration [mg/m ³ _n]		η [%]	H ₂ S concentration [mg/m ³ _n]		η [%]
			S_1	S ₂		S ₁	S_2	
	17.09.2003		206.0	71.0	65.5	242.0	60.0	75.2
1 / white	03.12.2003	23.07.2003	210.0	173.0	17.6	201.0	140.0	30.3
	05.03.2004		126.0	103.0	18.3	150.0	129.0	14.0
2 / red 16.09.20 10.11.20 14.12.20	16.09.2004	18.04.2004	276.0	128.0	53.6	334.0	136.0	59.3
	10.11.2004		201.0	96.0	52.2	189.0	103.0	45.5
	14.12.2004		120.0	72.0	40.0	118.0	45.0	61.9
	10.03.2005		105.0	102.0	2.9	128.0	81.0	36.7
	13.06.2005	2.06.2005	119.0	5.0	95.8	105.0	4.0	96.2
2.1	19.09.2005		179.0	100.0	44.1	160.0	104.0	35.0
5 / green	08.12.2005		275.0	239.0	13.1	323.0	251.0	22.3
	15.03.2006		212.0	157.0	25.9	223.0	185.0	17.0
4 / yellow	12.06.2006	13.05.2006	89.0	32.0	64.0	67.0	15.0	77.6
	22.09.2006		52.0	34.0	34.6	56.0	38.0	32.1
5 / blue	06.12.2006	9.11.2006	85.0	19.0	77.6	75.0	23.0	69.3
3 / blue	07.03.2007		109.0	73.0	33.0	100.0	66.0	34.0

Table 1

					=			
6 / black	19.06.2007	13.06.2007	84.0	17.0	79.8	80.0	16.0	80.0
	18.10.2007	16.10.2007	165.0	23.0	86.1	148.0	40.0	73.0
7 / grey	17.12.2007		136.0	62.0	54.4	126.0	56.0	55.6
12.03.2008		64.0	37.0	42.2	69.0	48.0	30.4	
8 / brown	17.06.2008	11.06.2008	123.5	4.9	96.0	119.0	7.6	93.6
8 / 010WII	16.09.2008		52.5	17.0	67.5	53.6	17.7	67.0
0 / orango	9.12.2008	22.11.2008	43.9	6.8	84.4	47.4	8.9	81.2
12.03.2009	12.03.2009		43.3	23.1	46.6	37.7	25.9	31.5
10 / violet	16.09.2009	18.06.2009	18.8	1.3	93.0	18.0	0.9	95.2
	9.12.2009		19.1	6.9	63.9	14.3	9.7	32.0
	average		124.6	64.1	54.1	127.4	64.4	53.8

S1, S2 - concentrations adequately - at the inlet and outlet, n - standard conditions: 273 K, 101.3 kPa, dry gas

Three types of trends were examined: second degree polynomial $(\eta = a \cdot \tau^2 + b \cdot \tau + 100)$, linear $(\eta = a \cdot \tau + 100)$ and exponential $(\eta = 100 \cdot \exp(a \cdot \tau))$, to determine the H₂S removal efficiency versus sorption time (τ). Regression coefficients (Table 3) taken for further analysis were determined as weighted averages after completion each series.

Regression coefficients

Function	Value				
	а	b			
Second-degree polynomial	0.00225	-0.726			
Linear	-0.374	-			
Exponential	-0.00682	-			



Fig. 1. Diagram of dissipation

Table 3

Reliability of regressions under analysis for describing time variability of desulfurization efficiency was evaluated using the following tools of statistical analysis: dissipation diagram, correlation coefficient, deviation of averages and relative deviation of averages, average deviation and relative average deviation. The dissipation diagram (Fig. 1) was made to evaluate the degree of overrating or underrating the results. The points with coordinates (η_{pi} , η_{oi}) were introduced into the diagrams. Theoretical points should lie along a straight line inclined at 45° and starting from the origin of co-ordinate system. The degree of dispersion with respect of this line is the measure of model accuracy.

The interdependence force of experimental data and those calculated by the model was

evaluated by means of correlation coefficient: $R = \frac{n \sum_{i=1}^{n} \eta_{pi} \eta_{oi} - \sum_{i=1}^{n} \eta_{oi} \sum_{i=1}^{n} \eta_{pi}}{n(n-1) \cdot \sqrt{V_p \cdot V_o}}, \text{ where } V_o \text{ and } V_o = \frac{1}{n(n-1)} \frac{1}{\sqrt{V_p \cdot V_o}}$

 V_p stand for variances calculated from

calculated from: $V_o = \frac{n \sum_{i=1}^n \eta_{oi}^2 - \left(\sum_{i=1}^n \eta_{oi}\right)^2}{n(n-1)}$ and

 $V_{p} = \frac{n \sum_{i=1}^{n} \eta_{pi}^{2} - \left(\sum_{i=1}^{n} \eta_{pi}\right)^{2}}{n(n-1)}, \text{ respectively, and } n \text{ represents successive numbers of}$

measurement series. The correlation coefficient is the measure of dependence between two data sets. If it is high (close to 1), the variables may be considered proportional.

Distribution of results with respect average values was evaluated by deviation of averages: $D_C = \frac{1}{n} \sum_{i=1}^{n} (\eta_{oi} - \eta_{pi})$. High, negative values of deviation prove the tendency of

underrating the results, high positive values show the tendency or overrating.

The relative deviation of averages: $W_C = \frac{D_C \cdot 100}{\frac{1}{n} \sum_{i=1}^n \eta_{pi}}$ was used to determine the percentage

of average level representing the deviation of averages in the distribution.

Average value of absolute deviations from their average values was evaluated by average deviation: $B_C = \frac{1}{n} \sum_{i=1}^{n} |\eta_{oi} - \eta_{pi}|$. It is the measure of data set variation. The lower is

the average deviation the better is concentration of measuring values around the average.

Relative average deviation: $O_C = \frac{B_C \cdot 100}{\frac{1}{n} \sum_{i=1}^{n} \eta_{pi}}$ was used to determine which percentage of

average level is the average deviation in the distribution.

The values of statistical analysis indexes for three versions of regression under consideration are summarized in Table 4. For comparison purposes, the version of ideal relation between calculated and measured efficiencies, *ie* when $\eta_{oi} = \eta_{pi}$, was presented.

Table 4

		Function			
Indicator	Reference value	Polynomial II deg.	Linear	Exponential	
Correlation coefficient R	1	0.79	0.90	0.96	
Deviation of averages D_C [%]	0	8.71	4.24	1.87	
Relative deviation of averages W_C [%]	0	12.93	6.30	2.78	
Average deviation B_C [%]	0	11.80	10.70	6.8	
Relative average deviation O_C [%]	0	17.54	15.86	10.14	

Values of model estimation statistical indicators

Results and discussion

Upon analyzing the indexes of statistical evaluation for regression versions under consideration (Table 4) and the dissipation diagram (Fig. 1), the exponential model was selected for further calculations. It was used to find the trend lines of H_2S absorption efficiency decline with sorption time which lines were then included into particular measurement series correspondingly to Table 2 (Fig. 2).



Fig. 2. Time changeability of H₂S removal efficiency for measurement series accordingly to Table 2

Trend lines for particular measurement series put on measurement points show no essential dependence between the sorption capacity decline and absorbed load of H_2S . Hence, it appears that apart from hydrogen sulphide there are other factors which deactivate the ore. Potentially, these are as follows:

 acidification of reaction environment by CO₂, which causes that H₂S binding mechanism is changed and ore sorption capacity declines (pH value of 8-10 is considered to be at the optimum level); acc. to [32], H₂S binding is hindered when acid reaction ore is used (elementary sulphur, which precipitates under such conditions, blocks the pores and impedes H_2S access to active iron compounds); likewise, sulphur presence may cause decline of ore sorption activity and colmatation the equipment;

- acidification of reaction conditions by decomposition of organic compounds contained in the ore (including sawdust);
- oxygen existing in biogas (average O₂ concentration was *ca* 0.05 % vol.), which causes that sulphides are oxidized to elementary sulphur;
- binding F⁺³ and Fe⁺² iron by CO₂, leads to creating iron carbonates and bicarbonates which can block the pores; reactions can proceed according to the following equations:

$$2Fe(OH)_3 + 3CO_2 \rightarrow Fe_2(CO_3)_2 + 3H_2O$$
(6)

$$Fe(OH)_3 + 3H_2S \rightarrow Fe(OH)_2 + S + 2H_2O$$
(7)

$$Fe(OH)_2 + 2CO_2 \rightarrow Fe(HCO_3)_2$$
 (8)

Verification and usage of the model

Model results of bed depletion time were compared with those from stoichiometric calculations and those from laboratory testing. The assumptions were that:

- the reaction of H₂S binding proceeds according to equations (2)-(3),
- concentration of H₂S in raw biogas, desulfurization efficiency, volumetric flow of biogas, volume and apparent density of the bed correspond to averaged values of these parameters for both desulfurization units over the full examination time (respectively: $S = 126.0 \text{ mg/m}_n^3$, $\eta = 54.0\%$, $L = 219 \text{ m}_n^3/\text{h}$, $V = 3.4 \text{ m}^3$ and $\rho = 941 \text{ kg/m}^3$),
- bed humidity and content of Fe_2O_3 and NaOH in the bed are at averaged levels from laboratory testing (respectively: w = 50%, A = 3.38% d.m., B = 22.91% d.m.).

In theory, considering exclusively the reactions with Fe₂O₃ ($m_{H2S I}$) and NaOH ($m_{H2S II}$), a single desulfurization unit can bind the following quantity of H₂S:

$$m_{H2SI} = \rho \cdot V \cdot \left(\frac{100 - w}{100}\right) \cdot \frac{B}{100} \cdot \frac{102}{160} = 235.4 \text{ kg}$$
$$m_{H2SII} = \rho \cdot V \cdot \left(\frac{100 - w}{100}\right) \cdot \frac{A}{100} \cdot \frac{34}{80} = 23.0 \text{ kg}$$

Hence, theoretical time of bed depletion, corresponding to average mass stream of absorbed H₂S ($m_{H2S} = L \cdot S \cdot \eta \cdot 10^{-8} \cdot 24 = 0.36 \text{ kg/d}$), is: $\tau_t = \frac{m_{H2SI} + m_{H2SI}}{I} = 717 \text{ d.}$

According to results of laboratory examinations (Table 1), the sorbent under consideration can absorb at least 0.1878 kg S/kg of bed dry matter, which corresponds to

the following time of complete exhaustion:
$$\tau_{l} = \frac{\frac{34}{32} \cdot V \cdot \rho \cdot \left(\frac{100 - w}{100}\right) \cdot 0.1878}{m_{H2S}} = 887 \text{ d.}$$

But, according to the regression model proposed, while assuming the minimum final efficiency $\eta = 5\%$, the maximum time of total bed exhaustion can be evaluated at 439 days which represents about 75% of theoretical time and 61% of that calculated from laboratory tests. Using the suggested model, it was also determined the expected efficiency of

desulfurization units at the moment of bed replacement, which - as averaged for all measurement series - was ca 20%, and also practical (maximum) operating time of the bed:

$$\tau_r = \frac{\ln \frac{20}{100}}{-0.00682} = 236 \text{ d} \text{ and practical absorbing power of bog ore:}$$
$$Q = \frac{L \cdot S \cdot \frac{\eta}{100} \cdot \frac{32}{34} \cdot 10^{-6} \cdot \tau_r \cdot 24}{V \cdot \frac{(100 - w)}{100} \cdot \rho} = 0.049 \text{ kg S/kg d.m. On this grounds, the bog ore}$$

consumption index for 1000 m_n^3 of purified biogas was found: $W_{ods} = \frac{V_r \cdot 1000}{8760 \cdot L} = 0.0028 \text{ m}^3/1000 \text{ m}_n^3$, where V_r - annual demand for bog ore for single

desulphurization unit: $V_r = \frac{365}{\tau_r} \cdot V = 5.3 \text{ m}^3.$

Conclusions

Calculations made for statistical coefficients proved that the exponential model provides the best representation of time variability of bog ore sorption capacity for H_2S . The sorption capacity found from this model, corresponding to practical operating period of the bed, is 0.049 kg S/kg of dry matter which represents about 26% of the capacity attained in laboratory (the difference may result from difficulties in maintaining the optimum operating conditions, such as pH value, temperature and humidity, for desulfurization units under real conditions).

The demand index for bog ore evaluated by the model proposed is $ca \ 0.003 \ \text{m}^3/1000 \ \text{m}^3_n$ of biogas, *ie* 2.6 kg/1000 m_n^3.

For the technology of sewage treatment and biogas treatment under consideration, the total time of bed depletion calculated by the model developed is 439 days while practical period of bed operation (*ie* till the efficiency is 20%) - 235 days.

Sulphur hydrogen is neither the just one nor the most important factor of bog ore deactivation. It is the carbon dioxide contained in biogas which seems to be the main factor of sorption capacity decline. Also the sawdust added to fluff the bed and oxygen present in biogas have an adverse impact on chemical mechanisms of H_2S absorption.

Considering the good points of biogas desulfurization with bog ore (*ie* availability and low purchase costs of the sorbent, simple operation and high availability factor of the plant) and its drawbacks (relatively low and time-variable efficiency of H_2S removal, arduous replacement of the bed, problems with waste disposal, limited potential of process automation and control, lack of market-available product with uniform and standardized properties, *eg* granulate) and also the effects attained (in general, biogas meets, after desulphurization, the specifications demanded by gas motor manufacturers), a statement could be made that, under Polish conditions, biogas desulfurization with bog ore is justified mainly due to economic reasons. However, the method needs further studies. Many authors draw attention to insufficient knowledge about sorption properties of bog ores and the sorption mechanisms as well.

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MODEL CZASOWEJ ZMIENNOŚCI ZDOLNOŚCI SORPCYJNEJ RUDY DARNIOWEJ

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Abstrakt: Na bazie wieloletnich (2003-2009), cyklicznych pomiarów składu biogazu powstającego z osadów ściekowych, na podstawie analizy statystycznej ich wyników opracowano model regresyjny opisujący czasowy charakter zmienności skuteczności odsiarczania biogazu za pomocą rudy darniowej. Model został zweryfikowany z wykorzystaniem obliczeń teoretycznych i wyników badań laboratoryjnych sorbentu. Za jego pomocą oszacowano czas wyczerpania i pojemność sorpcyjną złoża oraz wyznaczono wskaźnik zapotrzebowania na rudę darniową.

Słowa kluczowe: osad ściekowy, fermentacja, biogaz, odsiarczanie, analiza statystyczna, prognozowanie