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COMPARATIVE INVESTIGATIONS OF SEWAGE SLUDGE DIGESTION FROM THE CITIES OF GNIEZNO AND POZNAŃ

The run of methane fermentation of the sludge from the city of Gniezno has been investigated by periodic and continuous laboratory methods at 308 K. The sludge investigated contained excess amounts of chromium and sulphides if compared with the sludge from Poznań, whose fermentation in isolated digestion has not displayed any disturbances. An attempt has been made to elucidate the reasons of inhibitory action of toxic components in the process of digestion.

1. INTRODUCTION

Dynamic development of the industry in particular that of tannery in the city of Gniezno in the period of 1955–1970 has created a serious and ever increasing problem of sludge treatment. The wastewaters from the expanding tanning industry contributed to the decrease in the efficiency of the municipal wastewater treatment plant, and to the deactivation of the tricklingfilters. Excess of chromium, sulphides and calcium compounds in sludge distroyed the biological slime and a structure of the filter media [11].

The primary treatment part of a new municipal sewage treatment plant came into operation in 1973. The concentration of pollutants in raw sewage was maintained on a high level, despite a new installation for an in-plant preliminary treatment, such as equalization basin, drum saturators, settling tank and industrial sludge drying beds. At the oulet to the treatment plant the sewage BOD_5 varied from 440 to 1100 mg of O_2/dm^3, COD — from 884 to 1640 mg of O_2/dm^3, chlorides — 210–530 mg of Cl/dm^3, total suspensions — 280–1596 mg/dm^3, fats and mineral oils — 84–152 mg/dm^3 trivalent chromium — 2.8–3.3 mg of Cr/dm^3, sulphides — 5.8–14.6 mg of S/dm^3, phenols — 1.41–7.84 mg/dm^3 [13].

Sand sediments containing 25% of calcium, by weight, as well as large quantities of trivalent chromium and sulphides (mainly iron sulphides) were collected in a detritor of the municipal treatment plant [13].

Investigations of the efficiency of preliminary settling tank with a mechanical sludge collector have shown that in result of sedimentation of suspended solids, 68.6% of chromium from the sewage passes into sludges which are then pumped to nonheated, isolated digesters.

Both construction of the secondary treatment part of the municipal wastewater treatment plant and pilot-scale culture of activated sludge were started in 1975 [25].

According to the design, heated digesters will be also built, whereas the existing open digesters will be used as a second step of sludge digestion.

The purpose of the investigations was to establish the course of methane digestion of sludges from the town of Gniezno, characterized by a distinctly toxic composition, if compared with sludges from town of Poznań, which do not show any disturbances in normal conditions.

2. TOXICITY OF MINERAL COMPONENTS IN WASTEWATERS

Toxicity of metal ions is determined by their structure and physico-chemical properties. According to SEIFRITZ [23] the most important characteristics are: ionic mass, valency, electrochemical series, electronegativity ionic hydration, and ionic mobility adsorption capacity of ions, the two last features being the most essential from standpoint of toxicity. Hydration, the value of which is inversely proportional to atomic mass and to ionic radius, forms a kind of a protective envelope inhibiting ionic mobility.

INGOLS [5] attributes the phenomenon of toxicity to some disturbances in a cell metabolism which depend on the environmental factors and on time of contact with toxic compound. These disturbances, however, may have a reversible character and they need not lead to the death of cell. The literature data concerning the effect of the metal ions on anaerobic digestion of sludge are discordant and may evoke some objections.

According to Hoover copper ions in concentration of 0.5 mg/dm^3 copper in raw sludge do not affect the sludge digestion. Starting with the copper concentration of 1 mg/dm^3 inhibition of the process is observed, and at 3 mg/dm^3 copper it is entirely stopped [9]. Budgal has shown that the concentration of copper in sewage as low as 0.7 mg/dm^3 resulted in the accumulation of the metal in a raw sludge as high as 226 mg Cu/dm^3 (0.37% on a percent-of-solids basis) and caused a 11.3% decrease of gas production [9], whereas copper content in the sludge of 0.5% and 0.9% reduced the gas production by 35% and 50%, respectively [18].

BUCKSTEEG [4] has stated some ligher gas production decreases (by 15% and 60%, respectively, at copper contents of 0.4% and 0.8% on a percent-of-solids basis) as a result of copper hydroxide accumulation in the sludge.

On the other hand, MCDERMOTT et al. [17] have observed that even concentrations as high as 10 mg Cu/dm^3 in form of $CuSO_4$ in raw sewage, corresponding to 280 mg Cu/dm^3 in crude primary sludge, do not affect the anaerobic digestion of the sludge.

After Barnes and Braidech [9] the content of nickel in sludge as high as 500 mg/dm^3 decreases gas production by 10%, whereas according to BUCKSTEEG [4], 0.2%, 0.5% and 1% of Ni in the sludge solids reduce the gas production by 30%, 55%, and 70%, respectively.

The investigations have shown that insoluble iron compounds, such as oxides and hydroxides, have no effect on anaerobic digestion, whereas acid salts of iron, like $FeCl_4$, delay the biodegradation process [9].

RUDOLFS and AMBERG [22] have shown that solutions of sulphides at concentration higher than 50 mg/dm^3 S exert an inhibitory effect on anaerobic digestion resulting in 35% and 90% gas production decreases at sulphur concentrations of 80 mg/dm^3 and 250 mg/dm^3, respectively.

AULENBACH and HEUKELEKIAN [2] have found that insoluble sulphides, such as FeS, F_2S_3 and CaS do not inhibit the digestion within pH range 6.3–6.5. Of the soluble sulphides, such as Na_2S, $(NH_4)_2S$, H_2S, the highest toxicity has been stated for H_2S at pH 5.6.

From other investigations it follows that the toxic effect of dissolved salts of copper, lead, nickel, cobalt, and zink disappears as soon as these metals are precipitated in form of sulphides [8, 9, 18].

Lawrence and McCarty took advantage of the properties of sulphides [8], by feeding the digesters with sulphates, which in optimal conditions are reduced to sulphides neutralizing toxic effect of cations. Toxicity of heavy metals was manifested again when the sulphates were no more supplied.

In case of the simultaneous presence of several metal ions their toxic effect on bacteria is either intensified [4] or weakened, especially when there is an interaction of antagonistic cations [1, 8, 12, 15, 16].

ABELSON and ALDONS [1] while observing the growth of *E. coli* during digestion have stated an inhibitory effect of magnesium on toxic activity of Ni, Co, Cd, Zn and Mn ions.

Antagonistic interaction has been also stated among the ions of calcium, magnesium and sodium [12, 16]. LUBNER [12] while studying the antagonistic effect of Ca^{++} on Na^+ has shown that for the sludge whose salinity amounted to 10 g NaCl/dm^3 the optimal dose of calcium 2g $CaCl_2$/dm^3 yielded the increase in the efficiency of gas production from 85.3% to 93.7 with respect to the reference sludge sample.

MCCARTY and MCKINNEY have stated [16] that chlorides of alkali light metals exert a toxic effect on methane-producing organisms, which increases according to the following sequence (in equivalent concentrations) Ca^{++}, Mg^{++}, K^+, Na^+, NH_4^+. These authors have also stated [15, 16] that the toxicity of Na^+ depends on the accompanying anion the lowest being for CH_3COONa and NaCl, somewhat higher for $NaHCO_3$, and the highest for Na_2SO_4.

LUBNER [10] while investigating the effect of the brines from spa of Ciechocinek on the digestion of municipal sludges has stated that toxicity of saline water decreases with the increase in the temperature of biochemical reaction. The brines apart from their basic component (NaCl), contained also considerable amounts of calcium (2159 Ca/dm^3) as well as magnesium, strontium, barium potassium, lithium, manganese, aluminium, and iron combined with SO_4'', PO_4''', S'', Br', J', Cl'.

At the sludge salinity of 3% NaCl, the gas production at 285 K amounted to 48%, and at 305 K it increased to 59% with respect to the sludge containing no salinity.

Toxic effect of chromium — which is an amphoteric element and ist structure is particularly complex — is the least known of all the heavy metals. For bacteria and other low organisms the toxicity of hexavalent chromium is much higher than that of trivalent chromium. On the other hand, higher organisms, like fishes, are more sensitive to trivalent chromium [18].

SPANDOWSKA et al. [24] have stated, that in case of anaerobic digestion toxic dose of chromium^{+6} for acid-forming *E. coli* is 7 mg Cr/dm^3, and for *Pseudomonas fluorescens* it amounts to 3 mg Cr/dm^3. According to BRINGMANN and KÜHN [3] the threshold concentration of Cr^{+6} for *E. coli* is as low as 0.7 mg Cr/dm^3 and that of Cr^{+3} as high as 100 mg Cr/dm^3. PAGANO et al. [20] have demonstrated that the inhibitory effect of Cr^{+6}on methane digestion of acetic acid starts at the concentration higher than 1.5 mg Cr/dm^3. In short time, however, Cr^{+6} is reduced to Cr^{+3}, and then precipitated, hence the digestion is no longer delayed. According to these authors the inhibition of the digestion due to higher doses of Cr^{+3} is only transient, i.e. it lasts till the complete precipitation of chromium.

MOORE et al. [19] have found that at the daily dose of six-valent chromium, amounting to 50 mg Cr/dm^3 and applied in the process during 42 days, the gas production decreased to 11.5% with respect to the control. A single dose of 300 mg Cr/dm^3 resulted in a complete inhibition of gas production for 7 days, and the dose of 500 mg Cr/dm^3 caused the irreversible inhibition of gas production.

According to BUCKSTEEG [4] 0.1% concentration of Cr^{+6} in the sludge an a percent-of-solids basis results in the decrease of gas production by 35%, and 0.3% content of Cr^{+6} — by 55%.

According to Strell even 3% content of Cr^{+3} in the sludge on a percent-of-solids basis has no negative effect on biodegradation of organic substances [18]. Saboon et al. have established that the content of chromium^{+3} in fresh sludges cannot exceed 5 mg Cr/dm^3, [9].

Hoover and Wise, however, express the opinion that in fresh sludge the concentration of Cr^{+3} higher than 1 mg Cr/dm^3, is harmful for sludge digestion. At the concentration of Cr^{+3} equal to 200 mg Cr^{+3}/dm^3 the digestion decreases distinctly [9].

According to Vryburg dosage of 500 mg Cr^{+3}/dm^3 to the sludge after 10 days of digestion at 303 K reduces gas production by 50%, and the dosage of 1000 mg Cr^{+3}/dm^3 by 85% [9].

According to Polish regulations (Decree of the Prime Minister 29.11. 1975) the concentration of chromium in wastewaters discharged into municipal sewer system cannot exceed 0.2 mg Cr/dm^3, and the total concentration of heavy metals — 3.0 mg/dm^3. According to these regulations the admissible concentration of sulphides in municipal wastes amounts to 3 mg S/dm^3.

3. MATERIALS AND METHODS

The investigations of anaerobic digestion of sludge were performed under laboratory conditions in batch and continuous flow systems at 308 K, applying air thermostat. Fresh sludge after preliminary filtration through a sieve with mesh diameter of 4 mm, and heating up to the temperature of 308 K was introduced to a digester.

In the investigations using batch system preliminary thickened fresh sludges from primary settling tanks of the sewage treatment plants in Poznań and Gniezno were applied.

Their characteristics are given in table 1, series 1. As a seed the digested sludge (306–308 K) was used from separate digestion tanks (SDT) in Poznań.

Investigations in a flow-through system were conducted on sludges, whose characteristics are given in table 1, series 2. At the first stage of the process, they were seeded with digested sludge, from batch system.

Table 1

Characteristics of the sludges

Origin of sludges	Poznań		Gniezno	
Run No.	I	II	I	II
pH	6.8	6.9	6.6	6.8
Alkalinity meq/dm^3	36	32	51	47
Volatile fatty acids mg CH_3COOH/dm^3	648	450	792	720
Ammonium nitrogen mg N/dm^3	132	142	154	134
Phenols mg/dm^3	5.6	4.1	7.8	6.2
Water content %	93.89	93.14	94.16	92.93
Total solids %	6.12	6.86	5.84	7.07
— organic solids %	4.38	5.12	3.76	4.85
— mineral solids %	1.74	1.74	2.08	2.22
Organics, % (on percent-of--solids basis)	71.5	74.5	64.4	68.5
Mineral solids, % of solids	28.4	25.5	55.6	31.5
Sulphides, % S of solids	0.10	0.13	0.47	052
Calcium, % Ca of solids	—	3.32	8.35	7.18
Magnesium, % Mg of solids	—	0.72	—	1.38
Iron, % Fe of solids	2.14	2.45	3.66	3.37
Chromium, % Cr of solids	0.06	0.08	0.64	0.56
Copper, % Cu of solids	—	0.07	—	0.12
Nickel, % Ni of solids	—	0.04	—	0.08

The fresh sludge was stored in a refrigerator at the temperature of 275–277 K.

As a control parameter of the digestion process gas production at normal conditions (273K, 1000 hPa) was applied.

From the comparison of fresh sludges it follows that the respective contents of chromium sulphides, calcium, magnesium, and iron in the sludge from Gniezno are 9, 4, 2.5, 2 and 1.5 times higher than in those from Poznań, being, however, poorer in organic substances.

The investigations included also the sludge from Gniezno, extracted from isolated digesters operated at 287–291 K and at detention time 80 days. Its characteristics is the following: pH 6.7, volatile fatty acids — 2100 mg CH_3COOH/dm^3, solids — 9.52%, organics — 59.6%, sulphides — 0.52%, calcium 8.12% and three valent chromium $^{+3}$ — 0.71% Cr on a percent-of-solids basis.

4. RESULTS AND DISCUSSION

4.1. DIGESTION PROCESS IN A BATCH SYSTEM

The results of the anaerobic digestion of sludges has been presented in table 2, and in figs. 1 and 2.

From fig. 1 it follows, that anaerobic digestion process of the sludge from Gniezno city is inhibited with respect to the sludges from Poznań.

The parts of curves representing the adaptation period of methane bacteria are manifested in the decrease in gas production with respect to the starting point. For the sludge from Poznań the lag period is not very distinctly outlined (curve „*a*"), for the fresh sludge from Gniezno it is well pronounced and it covers the period from the first till the twelfth

Table 2

Daily (a) and total (b) gas productions fromt the fresh sludges, at 308 K, in cm^3/g of organics

Day of digestion	Fresh sludge from Poznań		Fresh sludge from Gniezno		Sludge from SDT from Gniezno	
	a	b	a	b	a	b
1	31.2	31.2	17.5	17.5	4.2	4.2
2	48.4	79.6	26.1	43.6	3.8	8.0
3	47.3	126.9	19.2	62.8	2.7	10.7
4	43.7	160.6	10.4	83.2	0.0	10.7
5	51.5	212.1	10.2	93.4	0.0	10.7
6	58.7	270.8	10.0	108.4	0.0	10.7
7	60.8	331.6	10.5	113.9	0.0	16.7
8	63.2	394.8	13.9	137.9	2.5	13.2
9	59.2	454.0	15.7	153.6	5.2	17.4
10	53.2	507.2	17.8	171.4	5.8	23.2
11	45.3	542.5	23.7	205.1	6.9	30.1
12	35.8	578.3	24.5	229.6	21.6	51.7
13	27.6	605.9	31.1	260.7	24.1	75.8
14	20.8	626.7	35.2	295.9	27.9	103.7
15	14.7	641.4	36.4	332.3	33.8	137.5
16	10.4	651.8	40.8	373.1	37.0	174.5
17	6.8	658.6	44.8	417.9	37.5	212.0
18	5.4	664.0	48.6	466.5	37.3	249.3
19	4.2	668.2	34.7	501.2	37.2	286.5
20	2.9	671.1	28.0	529.2	33.1	319.6
21	2.4	673.5	23.3	552.2	27.2	346.8
22	1.8	675.3	19.8	572.3	21.0	367.8
23	1.4	676.7	14.5	586.8	18.7	386.5
24	0.4	677.3	10.4	597.2	17.9	404.4
25	0.9	678.2	9.0	606.2	13.8	418.2
26	0.5	678.7	8.2	614.4	13.3	431.5
27	0.2	678.9	7.6	622.0	12.9	444.4
28	0.4	679.3	6.4	628.4	10.2	454.2
29	0.4	679.7	5.2	633.6	7.3	461.5
30	0.2	679.9	4.0	637.6	6.9	468.4
31			2.6	639.2	5.8	474.2
32			1.5	640.7	4.4	478.6
33			0.8	641.5	3.6	482.2
34			0.8	642.3	2.8	485.0
35			0.4	642.7	3.2	488.2
36			0.8	643.5	2.4	490.6
37			0.4	643.9	2.4	493.0
38			0.4	644.3	2.0	495.0
39			0.4	644.7	1.7	496.7
40			0.4	645.1	1.4	498.1
41					1.0	499.0
42					0.8	499.8
43					1.0	500.8
44					0.8	501.6
45					0.8	502.4

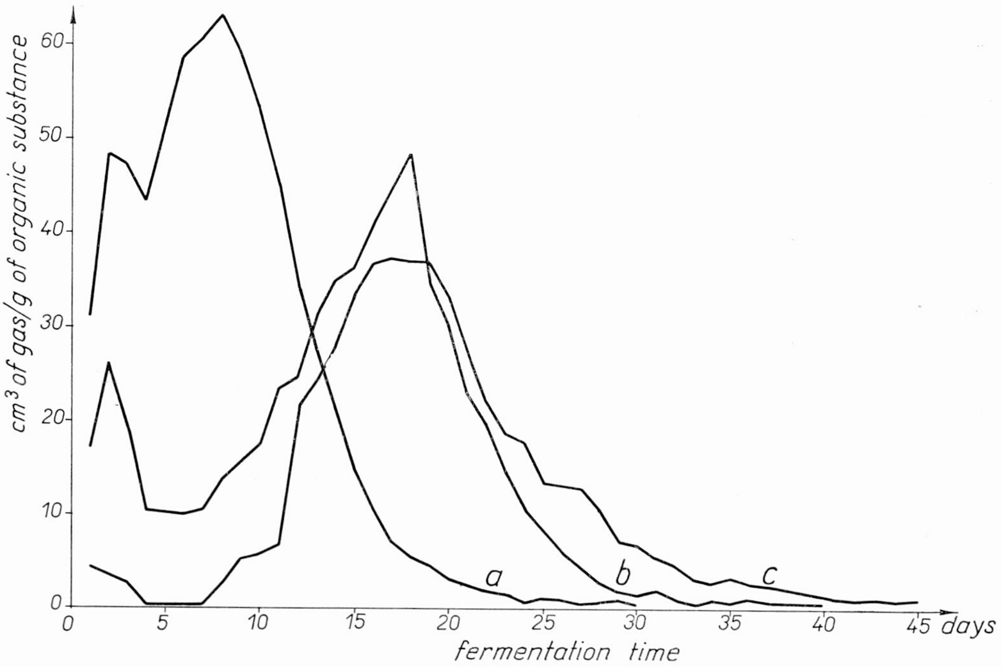

Fig. 1. Twenty-four hours increase in gas from the sewage sludge digestion at the temperature of 308 K

a — fresh sludge from Poznań, *b* — fresh sludge from Gniezno, *c* — sludge from SDT from Gniezno

Rys. 1. Dobowe przyrosty gazu z fermentacji osadów ściekowych w temperaturze 308 K

a — osad surowy z Poznania, *b* — osad surowy z Gniezna, *c* — osad z WKF z Gniezna

day of the digestion process (curve „*b*"), and for the sludge from isolated digesters a complete lack of gas production is observed for full 3 days (curve „*c*"). The rate of acclimated biomass growth exerts direct effect on the rate of biochemical reaction. For the sludge from Poznań the maximum gas production 63.2 cm^3 of gas per gram of organic solids, was reached as early as after 8 days, while for the fresh sludge from Gniezno the corresponding maximum value 48 g of gas per gram of organic solids was observed not earlier than after 18 days.

The cumulative curves of gas production in the digestion run of the sludges from Gniezno with respect to the sludge from Poznań are given in fig. 2. Final quantity of gas produced from the sludge „*c*", being lower with respect to the sludge „*b*", indicates that the latter was partially digested during its 80 day stay in isolated digesters.

The digestion time for a 90% of the total gas production, t_{90}, is equal to 13 days for the sludge from Poznań and 23 days for the sludge from Gniezno.

Assuming that the digestion of the sludges investigated proceeds according to the kinetics of the first order reaction, the reaction rate constant *k* can be determined from the equation:

$$G_t = G_e(1-10^{-kt}) \tag{1}$$

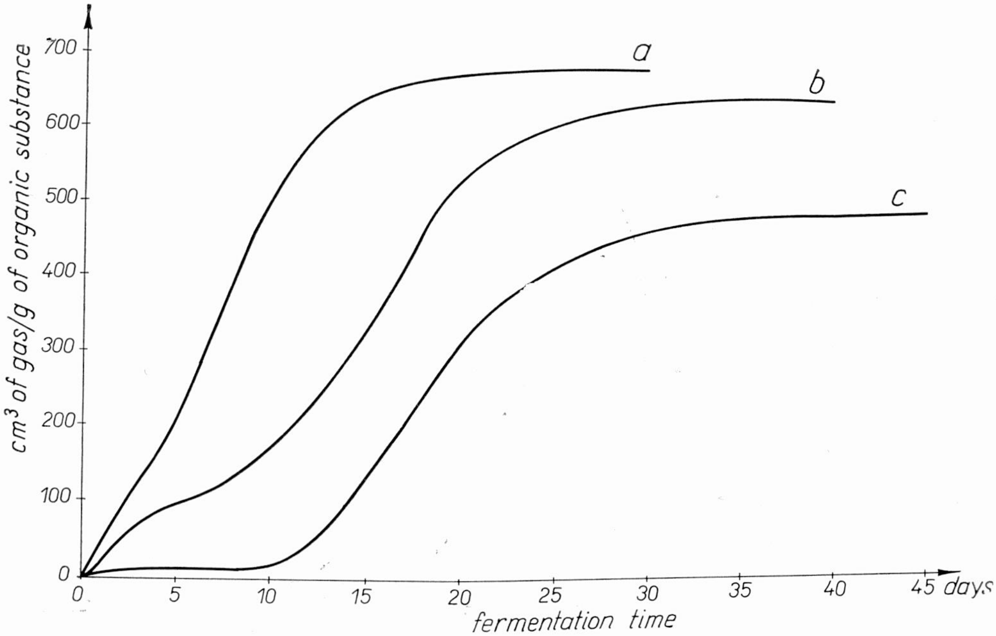

Fig. 2. Course of methane fermentation of sewage sludges at the temperature of 308 K
a — fresh sludge from Poznań, *b* — fresh sludge from Gniezno, *c* — sludge from SDT from Gniezno

Rys. 2. Przebieg fermentacji metanowej osadów ściekowych w temperaturze 308 K
a — osad surowy z Poznania, *b* — osad surowy z Gniezna *c* — osad z WKF z Gniezna

where

$G_t = 90\%$, quantity of gas produced after time t,
$G_e = 100\%$, quantity of gas produced after the digestion is completed,
t— duration of digestion.

Transformation of the eq. (1) yields:

$$k = \frac{1}{t} \log \frac{G_e}{G_e - G_t} = \frac{1}{t}. \tag{2}$$

The reaction rate constant values for sludges from Poznań and Gniezno are equal to 0.077 d^{-1} and 0.044 d^{-1}, respectively. Under optimal digestion conditions at the temperature of 308 K, the corresponding value of the rate constant for municipal sludge is usually 0.1.

During the digestion in a batch system the pH of medium varied between 6.6–7.5, i.e. within the optimal range for biochemical processes of this type.

It seems that in case of sludge from Gniezno, presence of large quantities of calcium and magnesium compounds, especially in form of carbonates and hydrocarbonates, is particularly advantageous because of their buffering properties in combination with gaseous CO_2 produced during digestion.

Partially soluble $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ play also an advantageous role as antagonistic ions with respect to ions of toxic metals occurring in sludges from the city of Gniezno [1, 12, 16].

4.2. DIGESTION PROCESS IN A CONTINUOUS FLOW SYSTEM

The process of continuous digestion was initiated in digested sludges, after the experiments performed by periodic method had been completed. The adaptation period of methane bacteria in case of toxic sludges from Gniezno was extended to 45 days. The averaged results from the digestion in a continous flow system are presented in table 3 for 4 different ranges of the digester loading.

Table 3

Characteristics of the digested sludges (averaged results)

Origin of sludges		Poznań				Gniezno			
Average residence time in a continuous flow system, d		25	16.7	12.5	10	25	16.7	12.5	10
Digester loading	volumetric %	4.0	6.0	8.0	10.0	4.0	6.0	8.0	10.0
	kg of organics/m^3 of digester. day	2.05	3.07	4.09	5.12	1.94	0.92	3.88	4.85
Gas production	m^3 of gas/kg of organics	0.560	0.530	0.490	0.438	0.470	0.440	0.395	0.310
	m^3 of gas/m^3 of digester. day	1.15	1.63	2.01	2.24	0.92	1.28	1.53	1.50
pH		7.6	7.5	7.3	7.1	7.4	7.1	6.3	5.8
Alkalinity meq/dm^3		63	63	64	66	68	69	71	74
Volatile fatty acids, mg CH_3COOH/dm^3		630	690	780	1020	960	1500	2280	3420
Water content %		87.45	87.96	88.52	89.28	88.88	89.38	90.06	91.14
Total solids %		12.55	12.04	11.48	10.72	11.12	10.62	9.94	8.86
— organic solids %		5.81	6.17	6.40	6.52	5.60	5.58	5.57	5.24
— mineral solids %		6.74	5.87	5.08	4.20	5.52	5.04	4.37	3.62
Organics, % of of solids		46.4	51.2	55.8	60.6	5.04	52.5	56.1	59.2
Mineral solids, % of solids		53.6	48.8	44.2	39.4	49.6	47.5	43.9	40.8
Biodegration of organics, %		70.5	64.1	56.6	47.5	52.7	49.0	40.8	24.6
CO_2 content in gas, volumetric %		22.8	23.6	25.2	27.4	25.4	27.2	30.8	36.6

For all the cases the degree of organics biodegradation was determined from the formula of Korolkov

$$R(\%) = \frac{100^2(b-a)}{b(100-a)} \tag{3}$$

where

a — % of mineral solids in total solids of fresh sludge,
b — % of mineral solids in total solids of digested sludge.

Table 4

Chemical characteristics of the sludge stored in a basin of the former lake Bielitko in Gniezno

Sampling depth, m		0.3	2.0
Specific density	g/cm^3	1.19	1.07
Colour		gray	black
Smell		eastry	bitumic
pH	pH	7.8	7.3
Acidity	meq/kg	10.0	12.0
Alkalinity	meq/kg	1500	420
Water content	%	66.81	76.36
Total solids	%	33.19	23.64
Organics, % of solids		33.04	38.78
Mineral solids, % of solids		66.96	61.22
Total nitrogen, % N of solids		1.77	1.76
Total phosphorus,% P of solids		0.68	0.60
Potassium,	% K of solids	0.08	0.21
Calcium,	% Ca of solids	19.26	10.75
Iron,	% Fe of solids	3.82	3.56
Natrium,	% Na of solids	0.24	0.40
Trivalent chromium,	% Cr of solids	1.56	0.58
Copper,	% Cu of solids	0.14	0.11
Nickel,	% Ni of solids	0.09	0.06

From the shape of curves (fig. 3) it follows that in the case of sludge from Poznań the gas production for 1 kg of organics in fresh sludge, decreases regularly with the increasing loading of the digester (curve A_1), and it increases (curve B_1) if the factor is calculated for unit volume of the digester. It is of a great importance from the technological point of view and it is worth noticing that even at the highest loading applied (10%) the gas production curve still shows increasing tendency. It should be also emphasized that at the volumetric loading of 4% i.e. at the average digestion time 25 days (table 3), the biodegradation degree of organics was high (70.5%) and in agreement with the empiric data according to KEEFER [6].

Despite the fact that the increase in digester loading results in a gradual decrease in the pH value and in the decrease in the degree of the organics degradation, the digested sludges have favorable characteristics from standpoint of dewatering.

In case of fresh sludge from Gniezno, a regular decrease in the gas production with the increasing loading of digester is however, observed solely within the range of low loadings. For higher loadings the drop in gas production for 1 kg of organics, has a progressive character („A_2"), and the biodegradation degree decreases down to the value of 24.6% (table 3).

The effect of overloading is also expressed by curve B_2 showing a characteristic maximum of the volumetric gas production (calculated for unit volume of the digester) at the

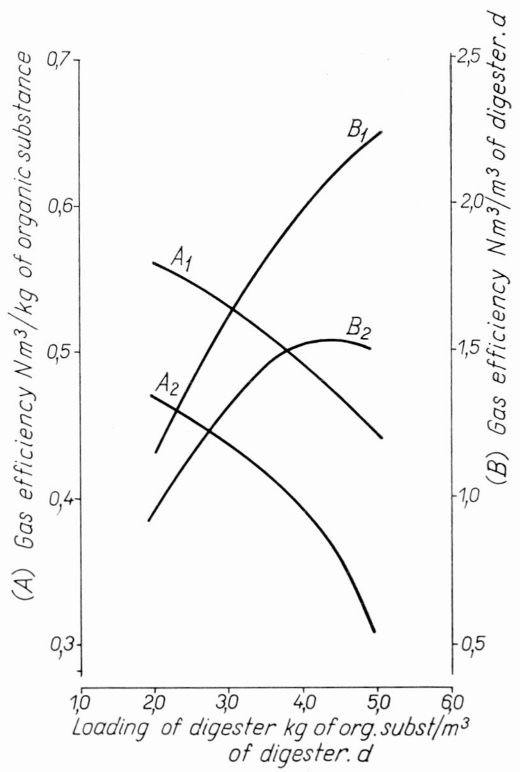

Fig. 3. Efficiency of gas from continuous fermentation of fresh sludges at the temperature of 308 K

A_1, B_1 — sludge from Poznań, A_2, B_2 — sludge from Gniezno

Rys. 3. Wydajność gazu z fermentacji ciągłej osadów surowych w temperaturze 308 K

A_1, B_1 — osad z Poznania, A_2, B_2 — osad z Gniezna

loading of 8% and it drops at higher loadings. Hence, it follows that the digestion of sludge from Gniezno can be conducted solely at the low digester loadings.

At the volumetric loading of 4%, i.e. at the average of digestion time of 25 days, the degree of organics degradation amounted to 52.7% (table 3), whereas, according to Keefer for 68.5% of organics in total sludge solids (table 1), it should be within the range from 62 to 64% [21].

At high digester loadings the digested sludge from Gniezno has disadvantageous properties.

At the digester loading of 10% the concentration of volatile fatty acids increase up to 3420 mg CH_3COOH/dm^3, and pH decreases down to 5.8. The excess of the acids gives the evidence to the violation of the balance between complex metabolism of saprophytic acid-forming bacteria, (such as *E. coli*, *Pseudomonas fluorescens*, *Bacillus subtilis*) and methanogenic bacteria, (such as *Methanobacterium suboxydans*, *Mathanobacterium proprionicum*, *Methanococcus mazei*). Methane bacteria, characterized by lower population and a higher sensitivity to the sludge overloading and toxic agents, can hardly cope with the processing of fatty acids, aminoacids and other compounds produced by sparophytic bacteria which are more resistant to external conditions.

With the increasing digester loadings and toxic components concentrations the gas production decreases, and moreover content of CO_2 in the gas increases at the cost of methane. This is due to the fact that, first of all, the activity of bacteria metabolizing higher volatile fatty acids, (such as valeric acid, and butyric acid characterized by a high methane-forming ability) is inhibited [6, 12, 14, 21]. Results of investigations indicate that the decreasing pH value is accompanied by the raise in toxicity of sulphides, heavy metals, and in particular of amphoteric chromium, which show an increasing tendency to pass from insoluble into ionic form considered to be toxic [2, 8, 9, 17, 20, 22, 28].

Due to the technological processes in tannery, and to some secondary processes in the sewage system of Gniezno, considerable amounts of chromium precipitate in form of $Cr(OH)_3$ at pH range 7–10. For pH value lower than 7 amphoteric $Cr(OH)_3$ shows the tendency to be transformed into soluble chromium salts, while for the pH value higher than 10 it may form soluble chromates. Under advantageous conditions $Cr(OH)_3$ is gradually dehydrated and transformed into insoluble and more stable oxide (Cr_2O_3) [11]. Thus it seems possible that at pH > 7 chromium in the digester occurs in the form of stable and possibly non toxic Cr_2O_3 and in form of unstable $Cr(OH)_3$, whereas at pH < 7 in result of the reaction with acetic acid (product of saprophitic bacteria) $Cr(OH)_3$ may pass into soluble and toxic chromium acetate $Cr(C_2H_3O_2)_3$.

Thus, it should be concluded that the toxicity of chromium depends on actual content of unstable chromium in form of $Cr(OH)_3$, and on pH rather than on the total content of chromium in the sludge. The sludge may also contain toxic chromium in the form of $CrPO_4$ which is soluble in acetic acid.

Toxicity of sulphides occurring in digester chiefly in form of FeS and Fe_2S_3 [13] depends, first of all, on the pH. The concentration of toxic H_2S increases with the decreasing pH values [2].

It should be also expected that iron ions will be activated toxically with the decomposition of iron sulphates which at low pH are unstable [9].

Copper and nickel sulphate appearing in relatively small quantities should not play any significant role as toxic agents, because of their high stability in form of GuS and NiS in acid solutions.

Sludges from Gniezno stored for many years in the basin of the former lake Bielitko were the subject of the investigations conducted since 1965 by former Institute of Local Economy in Poznań. The investigations were aimed at agricultural usage of the sludges.

The sludge samples taken from the lake at the depths up to 2 m contained 23.64% to 33.19% solids, as well as 27–50% of calcium as, calcium carbonate, 1.77% of nitrogen, 0.60%–0.68% of phosphorus, and 0.58–1.56% of chromium on percent-of-solids basis (table 4).

Because of so high content of chromium the sludge was not recommended for agricultural usage.

5. CONCLUSIONS

1. In fresh sludge from Gniezno the contents of chromium Cr^{+3} (0.56–0.64% Cr on percent-of-solids basis), sulphides (0.47–0.52% S), calcium (7.18–8.33%), magnesium (1.38%), iron (3.37–3.66%) are respectively 9, 4, 2.5, 2 and 1.5 times higher than those in the sludge from Poznań. The excessive concentrations of chromium and sulphides in the sludge of Gniezno are due to the low efficiency of the industrial wastewater treatment plant installed in the tannery.

2. During the digestion at 308 K in a batch system the maximal daily gas production from the sludge of Poznań (63.2 cm^3/g of organics) was attained after 8 days of the process, whereas that for the sludge from Gniezno (48.6 cm^3/g of organics) was reached as late as after 18 days. Digestion time for 90% of the total gas production amounted to 13 days and 23 days for the fresh sludges from Poznań and Gniezno, respectively.

3. In continuous flow system the gas output from the sludges of Poznań decreased regularly, with the increasing loading of the digester, from 0.560 m^3/kg of organics at residence time 25 day — to 0.438 m^3/kg of organics, at residence time 10 days. At the same time the daily outputs of gas, at the same load range, increases from 1.15 m^3/m^3 of the digester to 2.24 m^3/m^3 of the digester.

4. In a continous flow system, the gas production from sludge of Gniezno decreases with the increasing loading of digester from 0.470 m^3/kg of organics, at residence time 25 days, to 0.310 m^3/kg of organics, at residence time 10 days. At the same time the daily gas outputs increase from 0.92 m^3/m^3 of the digester to 1.53 m^3/m^3 of the digester at a residence time 12.5 days. The increase in a digester loading results in the drop in the volumetric gas output. For these reasons the full-scale digestion process of sludge from Gniezno should be conducted at low digester loadings.

5. Toxicity of trivalent chromium depends more on the content of chromium in unstable forms ($Cr(OH)_3$ and $CrPO_4$) at low pH, rather than on the total content of the element.

6. Toxicity of sulphides occurring in digesters mainly in form of FeS and Fe_2S_3 depends above all on the pH. With the decreasing pH values the concentration of toxic H_2S increases.

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BADANIA PORÓWNAWCZE NAD FERMENTACJĄ OSADÓW ŚCIEKOWYCH Z GNIEZNA I POZNANIA

Przeprowadzono badania laboratoryjne nad przebiegiem fermentacji metanowej osadów z Gniezna zawierających nadmierne ilości chromu i siarczaków w porównaniu z osadami z Poznania, których przebieg fermentacji nie wykazał zakłóceń w WKF.

Wykazano, że podczas fermentacji periodycznej w temperaturze 308 K maksymalny dobowy przyrost gazu w osadzie z Poznania wynosi 63,2 cm^3 na gram substancji organicznej po 8 dobach procesu, natomiast w osadzie z Gniezna maksymalny przyrost gazu w ilości 48,6 m^3/g następuje dopiero po upływie 18 dób. Techniczny czas fermentacji odpowiadający 90% wytworzonego gazu dla osadu z Poznania wynosił w konsekwencji 13 dób, natomiast dla osadu z Gniezna 23 doby.

W warunkach procesu fermentacji metodą ciągłą, wydajność gazu z osadu Poznania obniża się wraz ze wzrostem obciążenia komory od wartości 0,560 m^3/kg subst. organ., przy 25 dobach przebiegu, do 0,438 m^3/kg, przy 10 dobach przebiegu, i jednocześnie w zakresie tych obciążeń wzrasta wydajność dobowa gazu od 1,15 m^3/m^3 komory do 2,24 m^3/m^3 komory. Wydajność gazu z osadu z Gniezna obniża się ze wzros-

tem obciążenia komory od 0,470 m^3/kg subs. organ., przy 25 dobach przebiegu, do 0,310 m^3/kg, przy 10 dobach przebiegu, a jednocześnie wzrasta od 0,92 m^3/m^3 komory i dobę do 1,53 m^3/m^3 komory i dobę przy 12,5 doby przebiegu fermentacji. Większe obciążenie komory powodują spadek wydajności gazu również w przeliczeniu na m^3 komory. W warunkach technicznych istnieje więc możliwość prowadzenia fermentacji osadów z Gniezna tylko przy małych obciążeniach WKF.

Z przeprowadzonych badań wynika, że stopień toksyczności chromu trójwartościowego zależy nie tyle od ogólnej zawartości Cr^{3+} w osadzie ile od aktualnej zawartości w komorze chromu nietrwałego w formie $Cr(OH)_3$ i $CrPO_4$ przy jednocześnie obniżonym odczynie pH. Stopień toksyczności siarczków występujących w komorze fermentacyjnej głównie w postaci FeS i Fe_2S_3 zależy przede wszystkim od odczynu pH. Wraz z obniżeniem wartości pH środowiska zwiększa się stężenie toksycznie agresywnego siarkowodoru.

VERGLEICHENDE UNTERSUCHUNGEN DER METHANFAULUNG VON ABWASSERSCHLÄMMEN AUS GNIEZNO UND POZNAŃ

Untersucht wurde im Labormaßstab die Methanfaulung zwei verschiedener Abwasserschlämme. Der Schlamm aus Gniezno (G) beinhaltet übermäßige Sulfide- und Chrommengen — im Vergleich zum Schlamm der Hauptkläranlage von Poznań (P).

Im stationären Versuch, betrug die maximale Gasausbeute beim anaeroben Abbau des Schlamme P nach 8 Tagen 63,2 cm^3/g org. TS bei 308 K, die Gasmenge aus dem Schlamm G aber nur 48,6 cm^3/g org. TS nach 18 Tagen. Die technische Faulgrenze (90% Gasausbeute) wird beim Schlamm P nach 13, beim Schlamm G nach 23 Tagen erreicht.

Im kontinuierlichen Prozeß, war die spezifische Gasmenge von der Faulraumbelastung abhängig. Für Schlamm P ergaben sich nach 10 Tagen 0,560 m^3/kg org. Substanz und nach 25 Tagen 0,438 m^3/kg, was einer Tagesmenge von 1,15 und 2,24 m^3/m^3 Faulraumvolumen entspricht. Für den Schlamm G betragen die entsprechenden Werte:

0,470 m^3/kg org. Substanz nach 25 d,
0,310 m^3/kg org. Substanz nach 10 d,
0,92 m^3/m^3d bei 25 d und
1,53 m^3/m^3d bei 12,5 d.

Höhere Belastungen wirken sich in einer Abnahme der spezifischen Gasmenge aus. Aus diesem Grunde, sollte man die Schlämme G nur bei niedrigen Faulraumbelastungen anaerob abbauen lassen. Die festgestelle Giftwirkung von Cr^{+3} hängt nicht nur von der Menge dieser Ionen, sondern auch von der Menge des bei niedrigem pH unstabilen $Cr(OH)_3$ und von der Konzentration des $CrPO_4$ ab. Die Giftwirkung der Sulfide, die grundsätzlich in den Formen von FeS und Fe_2S_3vorliegen, hängt ebenso von der Reaktion des Schlammes ab. Je kleiner der pH-Wert, desto höher steigt die Konzentration des toxischen H_2S.

СРАВНИТЕЛЬНОЕ ИССЛЕДОВАНИЕ БРОЖЕНИЯ ВОДОСТОЧНЫХ ОСАДКОВ ИЗ ГОРОДОВ ГНЕЗНО И ПОЗНАНЬ

Проведены лабораторные исследования процесса метанового брожения водосточного осадка из города Гнезно, содержащего, по сравнению с осадками из Познани, избыточное количество хрома и сульфидов, у которых брожение не обнаруживало помех в WKF.

Показано, что в ходе периодического брожения при температуре 308 К максимальное суточное приращение газа в осадке из Познани составляет 63,2 $см^3$ на 1 г органического вещества после 8 суток процесса, а в осадке из Гнезно максимальное приращение газа в количестве 48,6 $м^3г$ достигается только по истечении 18 суток. Технологическое время брожения, соответствующее 90% произведенного газа для осадка из Познани, составило в результате 13 суток, а для осадка из Гнезно — 23 суток.

В условиях процесса брожения по непрерывному методу производительность газа из познанского осадка снижается с ростом нагрузки камеры — от 0,560 $м^3$/кг органического вещества при 25 сутках процесса до 0,438 $м^3$/кг при 10 сутках; одновременно, в пределах этих нагрузок повышается суточная производительность газа от 1,15 $м^3/м^3$ камеры до 2,24 $м^3/м^3$ камеры. Производительность газа из гнезненского осадка снижается с ростом нагрузки камеры от 0,470 $м^3$/кг органического вещества при 25 сутках процесса до 0,310 $м^3$/кг при 10 сутках; одновременно, увеличивается суточная производительность газа от 0,92 $м^3/м^3$ камеры до 1,53 $м^3/м^3$ камеры при 12,5 суток процесса брожения. Более высокие нагрузки камеры вызывают снижение производительности газа также в пересчете на $м^3$ камеры. В технических условиях имеется, таким образом, возможность производить брожение осадков из Гнезно только при низких нагрузках WKF.

Из проведенных исследований вытекает, что степень токсичности трехвалентного хрома зависит не столь от общего содержания Cr^{3+} в осадке, что от содержания камере, в данное время, неустойчивого хрома в виде $Cr(OH)_3$ и $CrPO_4$ при одновремнно пониженном pH. Ядовитость сульфидов, присутствующих в биотермической камере, преимущественно в виде FeS и Fe_2S_3 зависит прежде всего от pH. С понижением значения pH среды повышается концентрация токсически агрессивного сероводорода.