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CONSTRUCTION CHEMICALS PRODUCTION WASTEWATERS TREATMENT. PART 1. SLUDGE FROM ONE-STAGE PRETREATMENT

OCZYSZCZANIE ŚCIEKÓW Z PRODUKCJI CHEMII BUDOWLANEJ. CZĘŚĆ 1. OSADY Z JEDNOSTOPNIOWEGO PODCZYSZCZANIA

Abstract: This section gives an overview of the results of the evaluation of sludge generated under conditions of full technological scale in three similar installations as a result of the use of single-stage, physicochemical pretreatment of mixed processing wastewater from the production of construction chemicals. The wastewater originated mainly from manufacturing water-based paints and silicone renders for façades of concrete structures and for interiors, adhesive mortars and glazes, protective and decorative plasters, gypsum finishing and putty coats, self-levelling compounds, as well as grouts and sealing coats. Sludge were separated due to coagulation and chemical precipitation and floatation thickening; their dewatering was conducted in filtering appliances in a form of open gravity bag filters or in a pressurized chamber filter press. For “non-anhydrous” samples of dewatered sludge obtained using PIX[®] based iron(III) or PAX[®] based aluminum coagulants, toxicity characteristic leaching procedures (TCLP) were carried out and using fractionation the risk assessment code (RAC) was determined. It was found that the sludge dewatered by gravity or pressure indicate a low risk (LR) against Cd, Cr, Cu, Ni, Mn, Pb and Zn. In accordance with the TCLP criteria, they were classified as non-toxic waste.

Keywords: sludge from construction chemicals production, sludge from one-stage physicochemical pretreatment, TCLP test, risk assessment code (RAC)

Introduction

Single-stage, physicochemical pretreatment of industrial wastewater from the production of construction chemicals using coagulation methods leads mainly to remove dispersed phases such as colloids and suspended solids [1, 2]. To achieve a final reaction within the scope of the precipitability of hydroxides and/or sparingly soluble salts of e.g. heavy metals and anions present in the investigated effluents, these contaminants can also be removed effectively in a form of thickened phase of sludge [1]. The manufacture of construction chemicals involves the generation of processing wastewater, the contamination load structure of which is determined by the parameters of chemical composition of target products, however, in multiple dilution, which is a result of water purification of production devices and plant areas [1]. Some of indicative values that characterise the raw wastewater are often elevated significantly due to a separate washing of component containers used in manufacturing processes [1-4]. The effluents from the production of such profile have alkaline pH and contain mainly dominating quantities of colloids and suspensions of varied fastness degree of these dispersions that, e.g. constitute an essential mass of post-processing sludge after their coagulation [2]. This is a function of quantity and type of core mineral components added at the stage of manufacturing the products [5-9]. In this group, there are predominating primarily the dispersions of such fillers as: chalk, kaolin, dolomite, titanium

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white, talk, silica dust and mica, constituting mostly the essential pool of colloid-suspension phase of the pollutant load contained in the tested wastewater [10-20].

Distinctly lower concentrations but still significant considering the selection of an optimal method of purification are the substances that originate from the so-called admixtures. In this group, the compounds recorded most frequently in the tested raw wastewater are sodium or magnesium lignosulfonates that originate from plasticisers. From the group of superplasticisers, the post-processing effluents may contain sulfonated naphthalene and melamine polycondensates, starch hydrolyzates and polycarboxyethers that are also eliminated using coagulation methods [21]. From the admixtures that accelerate setting of concrete - calcium nitrate or calcium chloride, and from hydrophobizing additives - calcium stearate [22, 23]. From air entrainers for the production of construction masses - synthetic surfactants and modified rosin resins of natural origin [24]. Colouring admixtures (pigments mainly) may be a source of heavy metals in the effluents (e.g. Cr, Cu, Ni and/or Ti) [25, 26]. In literature you can find a few methods of physicochemical pretreatment of processing wastewater from the productions mentioned above that use coagulating and flocculating systems [1, 2] and hybrid ones, in which biological methods on the second stage are used such as technological variants of the methods of activated sludge or rotating biological contactor (RBC) [27]. A secondary effect of the physicochemical pretreatment of wastewater from manufacture of construction chemicals are the sludge of chemical composition determined by the load of raw processing effluents.

The aim was to assess the risk on the basis of the analysis of fractional composition of selected heavy metals and TCLP leachability tests for sedimentation sludge generated in a single-stage physicochemical pretreatment technological effluents, dewatered by thickening or using pressure in a chamber press. The sludge were generated in three similar pretreatment installations of full technological scale that were developed and implemented for physicochemical pretreatment of wastewater from the production of construction chemicals such as: water borne paints and silicone renders for the façades of concrete structures and interiors, cements and glazes, decorative gypsum finishing agents and putties, gypsum surfacers and putties, self-levelling compounds, as well as joint grouts and sealing masses [28].

Experimental part

Basic characteristics of the place of post-processing sludge generation and sampling

Sludge from physicochemical treatment of processing effluents were generated in a full scale single-stage wastewater pretreatment systems of daily outputs up to 12 m³ (installation A), 20 m³ (installation B) and 20 m³ (installation C) (Table 1) [28]. The processing systems were designed for the needs of mixed processing effluents from low-, medium- and high-tonnage production divisions of building industry chemicals [28]. In each case, the technological raw sewage (Table 2) gravity flown down to the retention basins, in which the averaging was carried out by means of pumps with bypasses. Basic treatment was done using coagulation in cylindrical-tapered reactors equipped with a slow-speed gate agitator. The sludge precipitated and thickened were pumped onto the appliances to dewater the sludge gravitationally (in the case of two installations: A and B); the appliances were bag filters or pressurized chamber filter press (installation C).

The dewatered groups of sludge were marked for each pretreatment installation in indexes A, B and C (Table 3).

Table 1
Basic characteristics of single-stage wastewater pretreatment installations

No.	Installation	Installation setup and pretreatment method [28] ^{a)}
1	A	<p>The installations included: a ground storage basins for raw effluents where their chemical composition was averaged by using pumps with bypasses, a central cylindrical-tapered processing reactor equipped with a slow-speed frame agitator, reagent metering stations, and a set for after-processing sludge dewatering.</p> <p>The course of physicochemical pretreatment:</p> <ul style="list-style-type: none"> • after filling the central reactor with averaged sewage under the conditions of continuous mixing, the acidic coagulant (PIX[®] 113 or PIX[®] 122 or PAX[®] 16) was metered directly onto the reactor in such doses to achieve the final value of pH = 8.0-8.5; • after coagulation stage, if necessary, the reaction corrections were made by metering aqueous solution of 10% NaOH or aqueous solution of 7.5% H₂SO₄ directly onto the reactor to achieve the final value of pH during minimum 30.0 minutes of continuous mixing; • the flocculation was conducted by metering 0.3% solution of flocculant 8398 Optifloc Cytec Industries Inc. Kemipol Sp z o.o., directly onto the reactor; • sludge thickened by sedimentation in the reactor was drained off onto a set of open bag filters to dewater them gravitationally (Table 3).
2	B	<p>The installations included: a ground storage basins for raw effluents where their chemical composition was averaged by using pumps with bypasses, a preliminary tube reactor with metered acidic coagulant, a central cylindrical-tapered processing reactor equipped with a slow-speed frame agitator, reagent metering stations, and a set for after-processing sludge dewatering.</p> <p>The course of physicochemical pretreatment:</p> <ul style="list-style-type: none"> • the averaged sewage was pumped through the tube reactor, to which under turbulent flow the acidic coagulant (PIX[®] 111 or PIX[®] 113, or PAX[®] 16, or PAX[®] 18) was metered, up to the central processing reactor where its volume, when filled up, was mixed by circulation; <ul style="list-style-type: none"> • the entire volume, when preliminary coagulated, was horizontally circulatory cross-stirred intensely in the tube reactor using the slow-speed frame agitator in the central cylindrical-tapered reactor and in the vertical tube reactor during at least 60 minutes up to stabilise pH (when necessary, the pH corrections were made by metering to the tube reactor: 10% aqueous solution of NaOH or 7.5% aqueous solution of H₂SO₄ to obtain the final reaction at the level of pH = 8.0-8.5 during at least 30 minutes); • after the stage of mixing and pH stabilising, the flocculation was conducted by metering 0.3% solution of flocculant 8398 Optifloc Cytec Industries Inc. Kemipol Sp z o.o. directly onto the central reactor; <ul style="list-style-type: none"> • the sludge thickened in the reactor was drained off onto the set of open bag filters to dewater them gravitationally (Table 3).
3	C	<p>This process is development of installation B by an additional stage of deepen reduction of ammonia nitrogen (AN) using powdered natural zeolite (of particle size ≤ 300 μm) metered from a dispenser with a screw feeder in doses of 2.5-3.0 kg/m³ effluent; the feeder was installed on the central cylindrical-tapered reactor after the stabilisation of the final pH before the stage of flocculation. Thickened sludge was drained off onto the set of chamber filtering press to dewater them under pressure of 11-12 bar (Table 3).</p>

^{a)} the planned output was calculated for individual installations, respectively, for: A) 12.0, B) 20.0 and C) 20.0 m³/day

Table 2

Basic characteristics of raw effluents treated in the installations A-C

No.	Installation	Effluent origin	Characteristics ^{a, b)} (median) ^{c)}
1	A	Effluents disposed from the production of water-based paints and silicone plasters for the façades of concrete structures and interiors. In lower volume fraction of medium-tonnage production of mortar adhesives and glazes, protective and decorative plasters. Periodically from high-tonnage production of putties and grouts.	pH = 9.1-11.7 (10.4) TSS = 760.4-4409.3 (2905.7) COD = 604.9-3441.9 (2105.7) BOD ₅ = 166.1-504.5 (274.2) TN = 57.3-227.3 (147.9) TP = 11.4-32.3 (16.8)
2	B	Mainly from high-tonnage production of protective and decorative plasters, self-levelling compounds and gypsum putties. In the smaller volume fraction, from high-tonnage production of grouts and sealing coating masses. Periodically, the effluents disposed from the production of water-based paints and silicone plasters for the façades of concrete structures and interiors, as well as cements and glazes.	pH = 8.6-11.3 (10.6) TSS = 486.9-7644.7 (3095.6) COD = 1195.8-4202.4 (2866.3) BOD ₅ = 145.1-543.8 (310.7) TN = 49.0-186.7 (100.5) TP = 6.9-29.6 (20.6)
3	C	Generally, from high-tonnage production of grouts, putties, gypsum surfacers, plasters, cements, mortars and glazes. In lower volume fraction of production low-tonnage water-based paints and silicone plasters for elevation of the façades of concrete structures and interiors, protective and decorative plasters. Periodically from low-tonnage production of self-levelling compounds.	pH = 9.9-12.8 (10.9) TSS = 1016.5-5314.9 (4311.8) COD = 1061.1-4526.3 (3424.9) BOD ₅ = 127.0-739.4 (301.8) TN = 38.4-402.0 (181.9) TP = 12.8-65.4 (27.3)

^{a)} parameters: TSS, COD, BOD₅, TN and TP were given in [mg/dm³]; ^{b)} determined acc. to the following standards, respectively: pH [29], TSS [30], COD [31], BOD₅ [32], TN [33] and TP [34]; ^{c)} median ("middle value") (m_{1/2}) of the order: ½

Table 3

Established markings of after-coagulation sludge from installations A-C

No.	Installation	Coagulant ^{a, b)}	Sludge marking
1	A	PIX [®] 111 PIX [®] 113 PAX [®] 16	AC _(PIX 111) AC _(PIX 113) AC _(PAX 16)
2	B	PIX [®] 111 PIX [®] 113 PAX [®] 16 PAX [®] 18	BC _(PIX 111) BC _(PIX 113) BC _(PAX 16) BC _(PAX 18)
3	C	PIX [®] 111 PIX [®] 113 PAX [®] 16 PAX [®] 18	CC _(PIX 111) CC _(PIX 113) CC _(PAX 16) CC _(PAX 18)

^{a)} the sludge were obtained using commercial coagulants made by Kemira Kemipol, of detailed characteristics given in [35]; ^{b)} in each case, 0.3% aqueous solution of flocculant Optifloc 8398 (Cytec Industrie Inc. Kemipol Sp. z o.o.) was used to thicken the precipitated phases dispersed in the central reaction, and to consolidate them before directing them onto the filter press

Analytical methods

Testing specimens were sampled 7 days past final dewatering process, counting from the moment of pumping the last of raw sludge onto the filtering sets in the case of using open bag filters (installations: A and B), and directly after pressurized dewatering using frame filter press (installation C) (Table 3). Collected specimens of sludge were submitted to procedures of 5-stage sequential extraction acc. to Tessier's methodology [36] and TCLP (Toxicological Characteristic Leaching Procedure) [37], then the determination of concentrations of selected heavy metals [38].

Table 4

Stages of proceedings carried out in the TCLP, basing on [37]

No.	Stage	Characteristics of technical operations
1	I	Sampling of sludge of particles size < 9.5 mm, homogenising and sieving.
2	II	The reaction of sludge was checked: 96.5 cm ³ of distilled water was added up to 5.0 g of "non-anhydrous" sample and mixed for 5 minutes, and then pH was measured. When pH < 5.0, the extraction solution L no. 1 ^{a)} was used, and when pH > 5.0, 3.5 cm ³ of 1 M HCl was added. Then, the covered content was heated up to 50°C for 10 minutes. When cooled to room temperature, pH was measured to determine a type of extraction solution L. If pH < 5.0, extraction solution L no. 1 was applied ^{a)} . If pH > 5.0, the extraction solution L no. 2 was used ^{b)} .
3	III	Preparing the composition for extraction - for the determination of components were used: 100.0 g of "non-anhydrous" of sludge samples (S) in two repetitions to which a suitable extraction solution (L) as described in the second stage was added in relation of the liquid to solid sludge (S), respectively (L/S) = 20:1.
4	IV	Shaking at room temperature for 18.0 hours.
5	V	Separating the phases by filtering.
6	VI	Analysis of metals concentration in the filtrate with pH < 2 (acidifying with HNO ₃).

^{a)} extraction solution L no. 1 was a mixture of the following composition: 11.4 cm³ 80% HOAc + 128.6 cm³ 1.0 M NaOH and topped up with distilled water to 2.0 dm³, and its final reaction was at the level of the pH = 4.93 ± 0.05; ^{b)} extraction solution L no. 2 was prepared by diluting 11.4 cm³ 80% HOAc with distilled water up to 2.0 dm³ whereby its final reaction was at the level of pH = 2.89 ± 0.05

The analysis of fractional composition of selected metals according to Tessier's procedure

Dewatered sludge from installations A and B were submitted to sequential extraction consisting in determining five fractions in accordance with Tessier's basic procedure specified in item [36]. For the extraction, 100.0 g of "non-anhydrous" sludge in two replications was used. The extraction conditions were the same as specified in our other works [39-42].

Results and discussion

The processing effluents from the production of construction chemicals, from which sludge were separated using coagulation methods, mainly characterised by alkaline reaction (pH), high polydispersity due to the presence of predominant mineral entraining admixtures (Table 2). In addition, there were observed considerable differences and variability in viscosity and diversity of the loads of: TSS, COD, BOD₅, TN & TP, as well as the widths of span in numerical values of the ratios: BOD₅/COD, BOD₅(COD)/TN, BOD₅(COD)/TP

& TN/TP. These facts induced the necessity of their pretreatment and were reflected in a structure of separated sludge and in leachability levels of heavy metals from them. The diversity of load amounts in wastewater of this type results in general from both the chemical composition of produced goods and the presence of hydrophilic-hydrophobic compounds, primarily the presence and concentration of hydrophobizing, plasticizing and liquidizing admixtures, and the presence of surfactants and/or resins as well.

In the post-coagulation sludge, an essential part of their dry matter constituted the products of hydrolysis of Al(III) or Fe(III) generated when acidic coagulants were introduced into the alkaline environment of pretreated effluents. The increase in dry matter of post-coagulation sludge with reference to the dry matter of dispersed fractions determined in the raw effluents, was a function of the increase in the fraction of the products of transformation of aluminum(III) or iron(III), particularly in an initial phase of their formation. For aluminum, the sludge were generated by the structures of polynuclear hydrolysis products initiated, in turn, by the intermediate forms such as $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ [43-45] and/or $\text{Al}_8(\text{OH})_{20}^{4+}$ [46]. The weight fractions of hydrolysis products of Al(III) and Fe(III) are the function of the final pH of averaged mixture of raw wastewater and the final pH after the parallel processes of neutralization and coagulation, and this value, in turn, is a function of coagulant dose. This relation is unequivocal, the higher pH of raw effluents and the lower final pH after their physicochemical pretreatment, the higher fraction of hydrolysis products in the dry matter of post-processing sludge.

Table 5 presents the data achieved as a results from TCLP procedure for dewatered post-processing sludge using thickening method by gravity (installations A and B) and pressure filtration (installation C). Samples for the research were collected after seven days of gravity settling of sludge on the sets of open sack filters, counting from the moment of pressing the last volume of post-sedimentary sludge. For pressure filtration the samples were taken directly after dewatering in the filtration press. While filtering the sludge pH was recorded as well. In installation C, the process of main, pressure dewatering was preceded by averaging sludge from the pretreatment conducted in a vertical thickening tank equipped with a frame agitator, which it had also an impact on the homogenisation of their contents, especially for small portion of the effluents discharged from single production batches. The analyses showed low concentration levels of heavy metals leachable from the tested sludge. The highest concentrations were recorded in the case of sludge generated in installation A that was the simplest configurational solution composed of: a conventional batch reactor with a direct metering reagents per volume subjected to be processed. In this solution, the time necessary to carry out all unit operations and processes was relatively the longest since it was limited of a time necessary to achieve a stable level of final pH. This issue is especially complicated for generating additional amounts of suspensions as hydrolysis products of the metal of introduced coagulant. Then, the intense averaging under turbulent conditions and mixing time are the parameters that have a significant effect on stabilising pH and then this parameter induces the leachability level of heavy metals form the tested sludge. This issue is shown in Table 5, with the instances for which pH of filtrates exceeded limit level $\text{pH} \geq 9.8$ (sludge from installation A, in particular). Then, above all, the concentration of Zn was registered on relatively highest levels. It was probably due to leaching the mobile forms of this element of the following type: $[\text{ZnOH}]^+$, $[\text{Zn}(\text{OH})_3]^-$, $[\text{Zn}(\text{OH})_4]^{2-}$ etc. [47-49].

It is indicated by the analysis of fractional contents presented in Table 6 for the cases where mixing time was not optimal and the filtrates obtained from the sludge during their dewatering were characterised by $\text{pH} \geq 9.8$. It is pointed out that the correlation of higher leachability of Zn with reference to the rest of metals considering the composition of raw materials to produce construction chemicals, was not analysed. Our measurements indicate that high concentrations of suspension fractions not only prolong necessary averaging measured by the stability of pH but also may be an effective way of fixing residual amounts of mobile forms of heavy metals using the sorption on hydroxy and/or hydroxy(oxo) products of the hydrolysis of coagulant's metal. At the same time, it may lead to minimise the level of their leachability from final post-processing sludge.

Table 5

The test results from TCLP

Heavy metals [mg/dm^3]	Sludge	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Installation A	1. AC _(PIX 111)	ND	ND	<0.2	<0.2	<0.2	<0.2	0.40
	2. AC _(PIX 111) ^{a)}	ND	0.27	0.22	<0.2	0.29	<0.2	0.42
	1. AC _(PIX 111) ^{b)}	ND	ND	0.31	0.28	<0.2	0.12	1.29
	2. AC _(PIX 111) ^{c)}	ND	ND	ND	0.24	<0.2	0.22	1.11
	1. AC _(PIX 113)	ND	<0.2	ND	<0.2	<0.2	<0.2	0.44
	2. AC _(PIX 113)	ND	<0.2	<0.2	<0.2	<0.2	<0.2	0.28
	1. AC _(PAX 16)	ND	ND	<0.2	<0.2	<0.2	<0.2	0.28
	2. AC _(PAX 16)	ND	ND	<0.2	<0.2	ND	<0.2	<0.2
Installation B	1. BC _(PIX 111)	ND	ND	ND	0.63	<0.2	ND	<0.2
	2. BC _(PIX 111)	ND	<0.2	ND	0.32	0.24	0.11	0.27
	1. BC _(PIX 113)	ND	<0.2	ND	ND	ND	ND	<0.2
	2. BC _(PIX 113)	ND	<0.2	ND	0.23	ND	ND	0.78
	1. BC _(PAX 16)	ND	0.43	ND	0.31	0.21	ND	<0.2
	2. BC _(PAX 16) ^{d)}	ND	0.29	ND	0.35	0.29	ND	<0.2
	1. BC _(PAX 18)	ND	ND	ND	ND	<0.2	ND	ND
	2. BC _(PAX 18) ^{e)}	ND	ND	ND	ND	<0.2	ND	ND
Installation C	1. CC _(PIX 111)	ND	ND	<0.2	0.21	<0.2	ND	0.28
	2. CC _(PIX 111)	ND	ND	<0.2	<0.2	<0.2	<0.2	<0.2
	1. CC _(PIX 113)	ND	ND	<0.2	<0.2	<0.2	<0.2	0.22
	2. CC _(PIX 113)	ND	ND	<0.2	<0.2	<0.2	<0.2	0.44
	1. CC _(PAX 16)	ND	ND	<0.2	<0.2	<0.2	ND	<0.2
	2. CC _(PAX 16)	ND	ND	<0.2	<0.2	<0.2	ND	<0.2
	1. CC _(PAX 18)	ND	<0.2	<0.2	ND	ND	ND	<0.2
	2. CC _(PAX 18)	ND	<0.2	ND	<0.2	ND	ND	<0.2
Standard EPA ^{f)}		1.0	5.0				5.0	

ND - not detected; ^{a)-e)} in these cases pH values of filtrates from raw sludge were recorded at levels, respectively: 10.61, 9.81, 10.79, 11.04 and 10.47; ^{f)} EPA Standard - details were described in [37]

It was found that the investigated sludge were characterised by the low leachability level of: Cd, Cr, Cu, Mn, Ni, Pb and Zn, when the reaction values of filtrates measured while sampling specimens were recorded at levels $\text{pH} < 9.8$. It should be stressed that into the environment in which the sludge were generated placed, a reagent was introduced that supported the creation of mobile coordination forms of metals, which were chlorides as a part of used coagulants: PIX 111 (ferric coagulant), or PAX 16 or PAX 18 (aluminum chlorides and polychlorides). To make a more complete assessment, supporting analyses were made after 6 and 9 weeks from the date of sampling and it was found that the tested

sludge held in the air underwent autocementation and the leachability of the components showed a decreasing trend. A proof of this effect was the observed decrease in time of the conductivity level measured in the water used to leach the autocemented compounds.

A useful criterion of the environmental assessment of waste is Risk Assessment Code (RAC) that can be used to estimate i.a. the ability to introduce a specific metal into a hypothetical food chain [50-53]. This parameter is described as a percentage share of heavy metals in the fractions: exchange one and fixed with carbonates, and its significance is the greater the greater is the recorded content of tested metal in these fractions in relation to the others. A detailed description of criteria adopted using RAC was presented in [50]. In our research, the fractional contents in the extracts were analysed only for Zn leached from the sludge, the filtrate reaction of which while sampling was recorded at levels $\text{pH} \geq 9.8$ as well as in view of both the recorded noticeably higher concentrations of this metal and the ease of its determination. For such cases, the mobile fractions determined for Zn, including both the exchange and carbonate ones, were usually within the range of 0-10% with rare events of slightly above 10% of their total sum (Table 6). Therefore, it can be assumed that the analytically assessed, dewatered sludge from single-stage, physicochemical pretreatment line were of intermediate nature, on the border of low (LR 0-10%) and medium (MR 11-30%) risk for the aquatic environment due to the recorded concentration level of mobile forms of Zn for sludge, the filtrate pH of which were recorded during sampling were at levels above $\text{pH} \geq 9.8$. In the operation practice of this installation, there are the cases when in the whole volume of the reactor there are not achieved the optimal pH considering the assumed design values of pH at the final level of $\text{pH} \approx 8.0-8.5$. This is the case when the mixing time is too short or there is no pH correction using H_2SO_4 . Excessive alkalisng may also be obtained as a result of a significant participation of CaO and/or MgO content in the suspended mass of raw effluents and the intensive, turbulent agitation within the stipulated time interval that leads to dissolve these compounds in water and to form OH^- in an excessive amounts due to the following reactions of dissociation: $\text{Ca}(\text{OH})_{2(s)} \leftrightarrow \text{CaOH}^+ + \text{OH}^-$, $\text{CaOH}^+ \leftrightarrow \text{Ca}^{+2} + \text{OH}^-$ and similarly for $\text{Mg}(\text{OH})_{2(s)}$. The nature of the low risk (LR 1-10%) is a feature of "non-unhydrous" samples of sludge with reference to the other analysed metals, if the reaction of their filtrates are $\text{pH} < 9.8$, or closer to the levels by the design (pH approx. 8.0-8.5). On the basis of analyses carried out, the adopted indirect risk within the span of values near the border LR and MR of the potential introduction of the metals to a hypothetical food chain; it concerns only the samples of sludge that were obtained under conditions of full technological scale without keeping the principle of optimal mixing time and without obtaining optimal final pH of the filtrates (Table 6). It may be interpreted by inducing conditions for an increased solubility of the precipitated earlier forms of Zn and by the increase in the concentration of mobile forms of this metal in fractions: F1 and F2 in presence of more alkaline pH of the filtrate from the sludge, which under the conditions of high hydration may result in a higher level of their water leaching, e.g. during storage.

In accordance with US EPA, the toxic character of waste only for lead is strictly defined and it assumes a limit value of leachability. For this metal, the concentration limit is set at the level of 5.0 mg/dm^3 [37]. For the investigated post-processing sludge from the single-stage physicochemical pretreatment of processing effluents generated in the production of selected construction chemicals, there were not recorded such levels of

concentrations of leached Pb. It should be noticed that, there were not recorded any significantly high concentrations of this metal also for randomly taken samples of the averaged raw wastewater (below 0.2 mg/dm^3). Therefore, the assessed sludge, regardless of the technique used for their dewatering, may be classified as non-toxic, because for randomly taken samples the criterion of Pb concentration at a level below the threshold of 5.0 mg/dm^3 in accordance with the TCLP scale suggested by US EPA, is met [37].

Table 6
Exemplary content [%] of zinc (Zn) in the individual fractions of 5-step sequential extraction made in compliance with Tessier's extraction method for samples of dewatered post-coagulation sludge from the treatment of effluents generated in the production of construction chemicals ^{a)}

Sludge	Filtrate reaction pH [-] ^{b)}	F1	F2	F3	F4	F5	RAC ^{c)}
1. AC _(PIX 111)	9.80	7.1	1.6	ND	ND ^{d)}	91.3	LR
2. AC _(PIX 111)	9.99	9.1	3.3	0.2	ND ^{d)}	87.4	MR
1. AC _(PIX 111)	10.81	8.2	2.1	0.9	0.7	88.1	MR
2. AC _(PIX 111)	10.89	6.8	3.1	1.7	2.1	86.3	LR
1. AC _(PAX 16)	10.64	7.6	2.5	0.7	0.2	89.0	MR
2. AC _(PAX 16)	10.70	9.2	2.4	0.8	1.3	86.3	MR
1. BC _(PAX 18)	9.96	4.7	1.2	ND	0.6	93.5	LR
2. BC _(PAX 18)	10.08	5.6	2.1	1.5	2.6	88.2	LR

^{a)} individual fractions were marked, respectively: F1 (exchangeable), F2 (carbonate), F3 (Fe-Mn oxides bound), F4 (organic) and F5 (residual); ^{b)} measurements of pH of the filtrate of raw sludge were made during the procedure of test sampling from the open bag filters (installation A and sludge marked with indexes AC, and installation B and sludge marked with indexes BC); ^{c)} MR - medium risk, LR - low risk; ^{d)} ND - not detected

Conclusions

Basing on the research, it was found that gravitationally dewatered pressurized post-coagulation sludge from single-stage physicochemical treatment of technological effluents generated in the production of constructional chemicals are particularly characterised by:

- very low leachability determined in accordance with the TCLP test procedure of metals such as: Cd, Cr, Cu, Mn, Ni, Pb and Zn and a low risk (LR) against these metals;
- comparable level of total and low concentrations of leachable metals, regardless of any technique of their dewatering when the filtrates from raw sludge have $\text{pH} < 9.8$;
- in the case of the optimal final reaction after neutralization and coagulation ($\text{pH} \approx 8.0-8.5$), and not exceeding the threshold value on the level of $\text{pH} \approx 9.8$, the leachability of Cd, Cr, Cu, Mn, Ni, Pb and Zn from the sedimentation sludge is at the level below 0.2 mg/dm^3 ;
- recorded increase in the concentration of leachable forms of Zn if the reaction of filtrates from raw sludge $\text{pH} \geq 9.8$; then the predominant speciation form of this metal make the residual fraction (F5).

Analysed sludge may be classified as non-toxic waste with reference to Pb and Cd, Cr, Cu, Ni or Zn (which are not limited) in accordance with the TCLP criteria of US EPA. In view of the trend to their rapid self-cementation in the air and the decrease of total leachability level while solidification, it is well-based to consider their use of commercial character.

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References

- [1] Nasr FA, Doma HS, Abdel-Halim HS, El-Shafai SA. Chemical industry wastewater treatment. *The Environmentalist*. 2007;27(2):275-286. DOI: 10.1007/s10669-007-9004-0.
- [2] Nasr FA, Doma HS, Abdel-Halim HS, El-Shafai SA. Chemical industry wastewater treatment. *J Eng Appl Sci*. 2005;52(4):697-713.
- [3] Alvarez D, Garrido N, Sans R, Carreras I. Minimization-optimization of water use in the process of cleaning reactors and containers in a chemical industry. *J Clean Prod*. 2004;12(7):781-787. DOI: 10.1016/S0959-6526(03)00054-4.
- [4] Von Rybinski W. Physical aspects of cleaning processes. In: Johansson I, Somasundaran P, editors. *Handbook for Cleaning/Decontamination of Surfaces*, Vol. 1. New York, USA: Elsevier; 2007. ISBN: 9780444516640.
- [5] Ferraris CF, Obla KH, Hill R. The influence of mineral admixtures on the rheology of cement paste and concrete. *Cement Concrete Res*. 2001;31(2):245-255. DOI: 10.1016/S0008-8846(00)00454-3.
- [6] Ramachandran VS. *Concrete Admixtures Handbook, Properties. Science and Technology*. Park Ridge, NJ: Noyes Publications; 1995. ISBN: 9780815513735.
- [7] Ding KW, Cheng C, Hao YQ, Xia S. Calculation and analysis of the thermal performance of a new type of rock wool color steel sandwich board. *Adv Mat Res*. 2014;908:8-13. DOI: 10.4028/www.scientific.net/AMR.908.8.
- [8] Burgos-Montes O, Palacios M, Rivilla P, Puertas F. Compatibility between superplasticizer admixtures and cements with mineral additions. *Constr Build Mater*. 2012;31:300-309. DOI: 10.1016/j.conbuildmat.2011.12.092.
- [9] Irassar EF. Sulfate attack on cementitious materials containing limestone filler - A review. *Cement Concrete Res*. 2009;39(3):241-254. DOI: 10.1016/j.cemconres.2008.11.007.
- [10] Telesca A, Marroccoli M, Calabrese D, Valenti GL, Montagnaro F. Flue gas desulfurization gypsum and coal fly ash as basic components of prefabricated building materials. *Waste Manage*. 2013;33(3):628-633. DOI: 10.1016/j.wasman.2012.10.022.
- [11] Diamanti MV, Lollini F, Pedferri MP, Bertolini L. Mutual interactions between carbonation and titanium dioxide photoactivity in concrete. *Build Environ*. 2013;62:174-181. DOI: 10.1016/j.buildenv.2013.01.023.
- [12] Katz HS, Milewski JV. *Handbook of Fillers for Plastics*. Springer-Verlag US; 1988. ISBN: 9780442260248.
- [13] Pavlidou S, Paspaspyrides CD. A review on polymer-layered silicate nanocomposites. *Prog Polym Sci*. 2008;33(12):1119-1198. DOI: 10.1016/j.progpolymsci.2008.07.008.
- [14] Mittal V. Polymer layered silicate nanocomposites: A review. *Materials*. 2009;2(3):92-1057. DOI: 10.3390/ma2030992.
- [15] Alexandre M, Dubois P. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Mat Sci Eng R*. 2000;28(1):1-63. DOI: 10.1016/S0927-796X(00)00012-7.
- [16] Wypych G. *Handbook of Fillers*. 4th Ed. Toronto, Canada: ChemTec Publishing; 2016. <https://www.sciencedirect.com/science/book/9781895198911>.
- [17] Paul DR, Mark JE. Fillers for polysiloxane ("silicone") elastomers. *Prog Polym Sci*. 2010;35(7):893-901. DOI: 10.1016/j.progpolymsci.2010.03.004.
- [18] Zhu W, Gibbs JC. Use of different limestone and chalk powders in self-compacting concrete. *Cement Concrete Res*. 2005;35(8):1457-1462. DOI: 10.1016/j.cemconres.2004.07.001.
- [19] Wang X, Shui Z, Yu R, Bao M, Wang G. Effect of coral filler on the hydration and properties of calcium sulfoaluminate cement based materials. *Constr Build Mater*. 2017;150:459-466. DOI: 10.1016/j.conbuildmat.2017.05.194.
- [20] Ahmed NM, Selim MM. Innovative titanium dioxide-kaolin mixed pigments performance in anticorrosive paints. *Pigm Resin Technol*. 2011;40(1):4-16. DOI: 10.1108/036994211111095883.

- [21] Voitovich VA. Cement-polyvinyl-acetate adhesives: An alternative to dry mortar. *Polym Sci D*. 2009;2(2):88-91. DOI: 10.1134/S1995421209020051.
- [22] Lin CL, Tsai MC. The effect of different calcium compound additives on the distribution of bottom ash heavy metals in the processes of agglomeration and defluidization. *Fuel Process Technol*. 2012;98:14-22. DOI: 10.1016/j.fuproc.2012.01.021.
- [23] Silva I, Castro-Gomes JP, Albuquerque A. Effect of immersion in water partially alkali-activated materials obtained of tungsten mine waste mud. *Constr Build Mater*. 2012;35:117-124. DOI: 10.1016/j.conbuildmat.2012.02.069.
- [24] Shi C, Qian J. High performance cementing materials from industrial slags - A review. *Resources Conserv Recycl*. 2000;29(3):195-207. DOI: 10.1016/S0921-3449(99)00060-9.
- [25] Wang N, He L, Egel E, Simon S, Rong B. Complementary analytical methods in identifying gilding and painting techniques of ancient clay-based polychromic sculptures. *Microchem J*. 2014;114:125-140. DOI: 10.1016/j.microc.2013.12.011.
- [26] Giustetto R, Gonella D, Bianciotto V, Lumini E, Voyron S, Costa E, et al. Transfiguring biodegradation of frescoes in the Beta Vergine del Pilone Sanctuary (Italy): Microbial analysis and mineralo-chemical aspects. *Int Biodeter Biodegr*. 2015;98:6-18. DOI: 10.1016/j.ibiod.2014.10.020.
- [27] Al-Ahmady KK. Effect of organic loading on rotating biological contactor efficiency. *Int J Environ Res Pub Health*. 2005;2(3-4):469-477. DOI: 10.3390/ijerph2005030012.
- [28] <http://www.projprzemeko.pl/realizacje/oczyszczanie-sciekow-przemyslowych.html>.
- [29] PN-EN ISO 10523:2012. Water quality - Determination of pH. <http://sklep.pkn.pl/pn-en-iso-10523-2012e.html>.
- [30] PN-EN 872:2007. Water quality - Determination of suspended solids - Method by filtration through glass fibre filters. <http://sklep.pkn.pl/pn-en-872-2007p.html>.
- [31] PN-ISO 15705:2005. Water quality - Determination of the chemical oxygen demand index (ST-COD) - Small-scale sealed-tube method. https://webstore.ansi.org/RecordDetail.aspx?sku=ISO%2015705:2002&gclid=Cj0KCQiAwKvTBRC2ARIsAL0Dgk2jF6M6tJb8RaZwYrYLizIpvVJusXfsRTx6TE0CHL5heM6oEpLskjkaAixlEALw_wcB.
- [32] PN-EN 1899-1:2002. Water quality - Determination of biochemical oxygen demand after n days (BOD) - Part 1: Dilution and vaccination method with the addition of allyl thiourea. <http://sklep.pkn.pl/pn-en-1899-1-2002p.html>.
- [33] CSN EN 16168. Sludge, treated biowaste and soil - Determination of total nitrogen using dry combustion method. <https://www.en-standard.eu/csn-en-16168-sludge-treated-biowaste-and-soil-determination-of-total-nitrogen-using-dry-combustion-method/?gclid=Cj0KCQi>.
- [34] PN-EN ISO 6878:2006. Water quality - Determination of phosphorus - Ammonium molybdate spectrometric method (ISO 6878:2004). https://www.en-standard.eu/din-en-iso-6878-water-quality-determination-of-phosphorus-ammonium-molybdate-spectrometric-method-iso-6878-2004/?gclid=Cj0KCQiAwKvTBRC2ARIsAL0Dgk15ROa9aFrrPzvYyYddXA3e9aG8CBYjxVWLSTfdUrIZJretN4RN9xYaAuyZALw_wcB.
- [35] <http://www.kemipol.com.pl/products>.
- [36] Tessier A, Campbell P, Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem*. 1979;51(7):844-851. DOI: 10.1021/ac50043a017.
- [37] US EPA. Test methods for evaluating solid waste. Physical/chemical methods. Method 1311. Toxicity characteristic leaching procedure (TCLP), EPA Publ. SW-846. 3rd ed. Vol. 1A. Office of Solid Waste and Emergency Response, US EPA, Washington, DC, 1992. <https://www.epa.gov/hw-sw846/sw-846-test-method-1311-toxicity-characteristic-leaching-procedure>.
- [38] PN-EN ISO 11885:2009E. Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885:2007). <https://pzn.pkn.pl/kt/info/published/9000128836>.
- [39] Rauckyte-Žak T. Comparison of the sequential extraction methods for soil subjected to the long-term effect of sewage. *Proc ECOpole*. 2015;9(2):489-497. DOI: 10.2429/proc.2015.9(2)057.
- [40] Rauckyte-Žak T. Assessment of sludges from rail freight car wash wastewaters. The primary sludges. *Proc ECOpole*. 2017;11(1):77-86. DOI: 10.2429/proc.2017.11(1)008.
- [41] Rauckyte-Žak T, Žak S. Wastewaters treatment from rail freight car wash. Assessment of physicochemical treated sludges. *Proc ECOpole*. 2017;11(1):87-96. DOI: 10.2429/proc.2017.11(1)009.

- [42] Żak S, Rauckyte-Żak T, Laurinavičius A. The influence of treated oleo-chemical wastewater applications on the metal speciation forms in soils. *J Environ Eng Landsc.* 2013;21(2):85-95. DOI: 10.3846/16486897.2013.773259.
- [43] Akitt JW, Greenwood NN, Khandelwal BL, Lester GD. ²⁷Al nuclear magnetic resonance studies of the hydrolysis and polymerisation of the hexa-aquo-aluminium(III) cation. *J Chem Soc Dalton Trans.* 1972;5:604-610. DOI: 10.1039/DT9720000604.
- [44] Bottero JY, Tchoubar D, Cases JM, Fiessinger F. Investigation of the hydrolysis of aqueous solutions of aluminum chloride. 2. Nature and structure by small-angle x-ray scattering. *J Phys Chem.* 1962;86(18):3667-3673. DOI: 10.1021/j100215a034.
- [45] Matijevic E, Mathai KG, Ottewill RH, Kerker M. Detection of metal ion hydrolysis by coagulation. III. Aluminum. *J Phys Chem.* 1961;65(5):826-830. DOI: 10.1021/j100823a028.
- [46] Amirtharajan A, Mills KM. Rapid-mix design for mechanisms of alum coagulation. *J Am Water Works Assoc.* 1982;74(4):210-216. <http://www.jstor.org/stable/41271001>.
- [47] Santos A, Alonso E, Callejón M, Jiménez JC. Heavy metal content and speciation in groundwater of the Guadamar river basin. *Chemosphere.* 2002;48(3):279-285. DOI: 10.1016/S0045-6535(02)00083-8.
- [48] Tonietto AE, Grassi MT. Speciation analysis of copper and zinc using differential pulse anodic stripping voltammetry. *Quim Nov.* 2012;35(1):170-174. DOI: 10.1590/S0100-40422012000100029.
- [49] Tonietto AE, Lombardi AT, Choueri RB, Vieira AAH. Chemical behavior of Cu, Zn, Cd, and Pb in a eutrophic reservoir: speciation and complexation capacity. *Environ Sci Pollut Res.* 2015;22(20):15920-15930. DOI: 10.1007/s11356-015-4773-3.
- [50] Perin G, Craboledda L, Lucchese M, Cirillo R, Dotta L, Zanetta ML. Heavy metal speciation in the sediments of northern Adriatic Sea. A new approach for environmental toxicity determination. In: Lakkas TD, editor. *Heavy Metals in the Environment*, vol. 2. Edinburg: CEP Consultants; 1985.
- [51] Sundaray SK, Nayak BB, Lin S, Bhatta D. Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments - a case study: Mahanadi basin, India. *J Hazard Mater.* 2011;186(2-3):1837-1846. DOI: 10.1016/j.jhazmat.2010.12.081.
- [52] Liang G, Zhang B, Lin M, Wu S, Hou H, Zhang J, et al. Evaluation of heavy metal mobilization in creek sediment: Influence of RAC values and ambient environmental factors. *Sci Total Environ.* 2017;607-608:1339-1347. DOI: 10.1016/j.scitotenv.2017.06.238.
- [53] Canuto FAB, Garcia CAB, Alves JPH, Passos EA. Mobility and ecological risk assessment of trace metals in polluted estuarine sediments using a sequential extraction scheme. *Environ Monit Assess.* 2013;185:6173-6185. DOI: 10.1007/s10661-012-3015-0.

OCZYSZCZANIE ŚCIEKÓW Z PRODUKCJI CHEMII BUDOWLANEJ. CZEŚĆ 1. OSADY Z JEDNOSTOPNIOWEGO PODCZYSZCZANIA

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Abstrakt: W tej części przedstawiono wyniki oceny osadów generowanych w warunkach pełnej skali technologicznej na trzech zbliżonych konfiguracyjnie instalacjach w wyniku zastosowania jednostopniowego, fizykochemicznego podczyszczania mieszanych ścieków technologicznych z produkcji chemii budowlanej. Ścieki pochodziły głównie z linii wytwarzania wodorozcieńczalnych farb i tynków silikonowych do elewacji konstrukcji betonowych i wnętrz, zapraw klejących i glazur, tynków ochronnych oraz ozdobnych, gładzi gipsowych i szpachlowych, zapraw samopoziomujących, a także mas fugowych i powłok uszczelniających. Osady wydzielano w wyniku koagulacji i strącania chemicznego oraz flokulacyjnego zagęszczania, a ich odwadnianie prowadzono na zespołach filtracyjnych, stanowiących otwarte grawitacyjne filtry workowe, lub na ciśnieniowej, komorowej prasie filtracyjnej. Dla „niebezwodnych” prób odwodnionych osadów uzyskiwanych koagulantami żelazowymi klasy PIX[®] lub glinowymi klasy PAX[®] przeprowadzono procedury wymywalności TCLP oraz ocenę ryzyka za pomocą frakcjonowania, stosując kod RAC. Stwierdzono, że odwodnione grawitacyjnie lub ciśnieniowo osady wykazują niskie ryzyko (LR) względem Cd, Cr, Cu, Ni, Mn, Pb and Zn. Zgodnie z kryteriami TCLP, sklasyfikowano je jako odpady nietoksyczne.

Słowa kluczowe: ścieki technologiczne z produkcji chemii budowlanej, osady z jednostopniowego podczyszczania fizykochemicznego, test TCLP, kod oceny ryzyka (RAC)