



Statistical appraisal of selected qualitative parameters of leachates from an industrial waste heap

Kazimierz Szymański^{a,*}, Bartosz Walendzik^a, Elżbieta J. Bielińska^b, Beata Janowska^a, Roksana Królak^a

^a*Koszalin University of Technology, Faculty of Civil Engineering, Environmental and Geodetic Sciences, Waste Management Department, ul. Śniadeckich 2, 75-453 Koszalin, Poland, Tel. +48 94 3478570; Fax: +48 94 3427652; email: kazimierz.szymanski@tu.koszalin.pl (K. Szymański)*

^b*University of Life Sciences in Lublin, Institute of Soil Science, Environment Engineering and Management, ul. Akademicka 13, 20-950 Lublin, Poland*

Received 15 November 2019; Accepted 21 December 2019

ABSTRACT

This paper is about the degree of contamination of land with mineral and organic compounds at a concrete manufacturing company site. Leachates from the site show alkaline reaction (pH > 12.0). Only effluents from the vehicle washing facility, which were collected in the sewer sump, had different pH. Leachates contain significant amounts of calcium (max. 407.53 mg/L). This pertains particularly to liquid effluents from the washing of truck concrete mixers providing alkaline pH in the sump. Effluents from the vehicle washing facility featured high organic carbon concentration, which had an impact on the increased level of (BOD - biological oxygen demand) BOD₅ and (COD - chemical oxygen demand) COD_{Cr}. The acceptable level of heavy metals concentration was not exceeded in leachates with the exception of lead and chromium compounds. Hexavalent chromium occurred mainly in samples 1 and 2 whereas trivalent chromium-in samples 3 and 4. This metal (in a trivalent form) occurred in the form of sparingly soluble compounds in sewage sludge and waste. Therefore, its ability to migrate in the environment was significantly reduced. The source of the metal was, possibly, some grades of cement. Cement could consist of ashes, blast-furnace slag and special additives containing chromium.

Keywords: Industrial waste; Leachates; Concrete elements; Heavy metals; Chromium

1. Introduction

Raw materials used for the production of cement contain a number of compounds of such heavy metals as chromium, lead, zinc, copper, nickel, cobalt and mercury. For example, Portland Cement 35 F may contain chromium compounds at 79 g Cr/t level. Other grades of cement may contain chromium compounds at approximately 120 g Cr/t level. Some sources indicate that chromium content in cement may reach even 200 g Cr/t level, including Cr⁶⁺ from several to 30 g Cr/t [1]. It is considered that the main source of chromium in cement is limestone and clays. In Poland, this element

occurs in limestone at approximately 9 g Cr/t level, whereas in clay—at 60 g Cr/t level. These are high values because, by comparison, hard coal from Polish mines, used as fuel, contains 25 g Cr/t on average [2]. In the cement manufacturing process performed at high temperature, in the presence of oxygen, the degree of chromium oxidation changes from Cr³⁺ to Cr⁶⁺. Therefore, the presence of this element as Cr⁶⁺ in clinker is much higher than in the raw material. Also, Cr⁵⁺ may occur at temperature values exceeding 700°C, whereas above 1,400°C it occurs also as Cr⁴⁺ [3,4]. Therefore, leachates from concrete elements production contain also toxic chromium compounds. They can form, in an aqueous environment, various chemical compounds including specific mineralogical

* Corresponding author.

structures [5–8]. It appears from research work on waste and leachates from construction materials production performed by the authors of this paper, as well as by other scientists, that depending on the composition of waste containing chromium and other elements, like barium, such compounds as BaCrO_4 (VI), Ba_3CrO_5 (IV), $\text{K}_2\text{Cr}_2\text{O}_7$ (VI), K_2CrO_4 (VI) may be formed. Chromium compounds may occur in sparingly soluble form, where chromium occurs as Cr^{3+} or as easily soluble compounds of Cr^{6+} . In aquatic environment, chromium can also produce aqua ions, complex ion or ion pairs [9,10]. In such conditions they assume, in most cases, a form of exchangeable, selectively adsorbed or interfacially precipitated ions [10]. For example, in the cement hydration process, some chromium compounds occur as calcium chromate CaCrO_4 (VI) and can be embedded into ettringite crystal lattice in the form of chromate-ettringite hydrate $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaCrO}_4\cdot32\text{H}_2\text{O}$. [11,12]. Mineral compounds of chromium in strongly alkaline medium, that are typical for leachates from a heap containing concrete and construction elements waste, can form sparingly soluble hydroxides - $\text{Cr}(\text{OH})_3$. At the same time, in strongly alkaline leachates, chromium compounds may produce ionic forms: $\text{Cr}(\text{OH})_2^+$ or $[\text{Cr}(\text{OH})_2(\text{H}_2\text{O})_6]^+$, which occur in soluble form. Reduced Cr^{3+} ions also tend to combine via oxygen bridges or hydroxide groups with other waste or leachate components. A number of polynuclear complexes, like a combination of chromium with carboxylic acids, are then formed, producing a compound of $[\text{Cr}_3(\text{CH}_3\text{COO})_6\text{O}]^+$ structure. Carboxylic groups may originate from humic compounds, which occur also in wastewater from combined sewerage systems. It appears from the research and literature studies performed that chromium compounds in leachates from waste heap occurred mostly in Cr^{3+} form thus being sparingly soluble, posing a considerably lesser hazard for the aquatic environment [2,9]. Definitely, the occurrence of chromium compounds in manufactured construction materials, therefore, in waste as well as waste leachates, originates from the use of various cement grades. Scientific papers comprise information that chromium content in Portland cement is approximately 79 mg Cr/kg [3,7]. Apart from chromium compounds, occurrence of lead in tested leachates was confirmed; this may result from various cement additives, including slag and ashes containing those elements.

This publication pertains to the issue of waste management in the technical concrete fabrication plant. Technical concrete and its prefab elements make a source of leachates. Waste from technical concrete and prefab elements production was deposited there next to the technological facilities and truck concrete mixers (Fig. 1 items 1&2). Washing of those facilities/devices generated leachates from deposited waste. The waste heap, which was located in the “open-air”, without any cover, was exposed to contact with rainwater and water flowing from the site. Therefore, the waste dump was a source of leachates creating a leachate pond. Some volume of those leachates was discharged to the combined general sewerage system mixing with municipal wastewater. Additionally, they put mineral and organic pollutants of various toxicity into the municipal wastewater. It appears from the research work performed in 2010 by some environmental protection institutions that chromium content in leachate deposits taken from a sump next to the truck concrete

mixer washing facility was 31.56 mg Cr/kg dry matter (DM), whereas in the sediment occurring near the concrete unit washing facility –6.10 mg Cr/kg DM was found. It appears from the earlier research work performed by authors of this paper during the period of 2014–2015 that leachates from the waste heap contained considerable amounts of chromium compounds (0.365 mg/L). The concentration of lead varied within 0.005–0.048 mg/L range. In the light of the applicable law pertaining to the conditions of discharge of wastewater contaminated with those compounds to waters or grounds, such wastewater should not be discharged (without preliminary pre-treatment) directly to the municipal wastewater sewerage system [13]. Tests repeated in 2019 indicated that in said leachates (Table 2, Sample No 5) total chromium concentration was at 0.022 mg/L, whereas lead-at <0.005 mg/L. Other heavy metals occurred in minute quantities, not posing any particular hazard for the aquatic environment [13,14].

The objective of this research work was an assessment of the hazards that the aquatic environment was exposed to from industrial leachates coming from construction waste heap. Leachates in question contained heavy metals, including toxic chromium compounds, and were discharged directly into the municipal sewerage system.

2. Tested material and methodology of research

2.1. Scope of research

The scope of research performed at the production site pertained to:

- Determination of primary physicochemical indicators of wastewater taken for tests from existing there sewerage system and leachates from the leachate pond located nearby the waste heap;
- Determination of heavy and alkaline metals in industrial leachates and in sumps.

The tests were performed during the period of 2014–2015, and repeated within a limited scope, in 2019. The leachate sampling points are illustrated in Fig. 1:

- Truck concrete mixer washing facility–sump No 1,
- Concrete production unit washing facility–sump No 2,
- Nearby former vehicle wash, next to the waste heap–piezometric borehole No 3,
- Industrial waste heap–piezometric borehole No 4.

Wastewater sediment samples taken from two sumps (No 1 and 2) were tested for chromium contents in 2010 by the laboratory of Provincial Inspectorate for Environmental Protection in Szczecin (Poland).

2.2. Analytical methodology

Particular determinations were performed in accordance with the Regulation of the Minister of Maritime Economy and Inland Navigation on substances that are particularly harmful to aquatic environment and conditions that must be complied with in discharging wastewater into waters or grounds as well as in discharging of rain water or meltwater



Fig. 1. Leachate sampling points at the industrial waste heap site.

into waters, or water facilities, dated 12 July 2019, O.J.L 2019, Section. 1311 [14] and the methodologies indicated in literature [15,16]. The scope of the research work is illustrated in Tables 1 and 2. Test results were compared with the acceptable concentrations of the indicators defined in the Regulation of the Minister of Housing on the accomplishment of industrial wastewater suppliers' duties and conditions for discharge of wastewater into sewerage systems dated 14 July 2006 O.J.L. No 136, Section 964 [13].

Table 2 shows the test results for heavy and alkaline metals, which were determined using the atomic absorption spectrometry (ASA) technique. Having on mind determination of heavy metals contents in leachate and leachate sediment samples, said samples were mineralized by a mixture of acids (65% HNO_3 , 70% HClO_4 and 30% H_2O_2) using microwave energy (Milestone 1200 Mega apparatus, Italy). Also, FAAS (iCE 3500Z Thermo Scientific SOLAAR, United Kingdom) technique was used for heavy metals determination [3,5].

2.3. Statistical treatment of the results

To evaluate the measures of tested sets of pollutants occurring in particular concrete production leachate samples, the STATISTICA package was used (multiple regression module) [17]. The objective of this analysis was the determination

of statistically significant impact of particular components (independent variables) on chromium concentration in the tested leachate. To describe the correlation between particular variables, an estimator of the coefficient of correlation between tested features, as correlation r , was used. For this purpose Fischer (F) test verifying the hypothesis that the multiple correlation coefficient is significantly different from 0, which means that at least one of the model structural parameters (without free term) differs from zero, was useful. This resulted in the development of a model taking into account selected, significant parameters of pollutants contained in leachates from the construction industrial waste heap based on the example of suspended matter and total solids in which high concentration of chromium compounds was found. Using this model it's check-up/verification will be performed.

3. Test results

Leachates were tested at the concrete and concrete elements production facility site. Industrial waste deposited there originated mainly from washing of technological devices/facilities/plant and truck concrete mixers. They had also direct contact with rainwater. Leachates generated there, discharged directly to the municipal combined sewerage system contained an increased amount of mineral compounds, including heavy metal compounds. Tests

Table 1
Results of physicochemical analysis of leachate samples

Parameter	Tests performed in the following years					Acceptable values [13,14]
	2014–2015				2019	
	Sample No.					
	1	2	3	4	5	
pH	7.66	12.02	12.60	12.59	12.8	6.5–12.5
Conductivity, $\mu\text{S}/\text{cm}$	318	1698	4560	6180	2450	–
Ammonium nitrogen, $\text{mg N-H}_4^+/\text{L}$	0.16	0.57	0.22	0.05	0.08	10
Nitrate nitrogen, $\text{mg NO}_3^-/\text{L}$	0.10	0.24	0.18	0.19	0.10	30
Nitrite nitrogen, $\text{mg NO}_2^-/\text{L}$	0.002	0.020	0.000	0.002	0.000	1
Kjeldahl total nitrogen, $\text{mg N}/\text{L}$	6.91	2.51	0.64	0.73	0.90	30
Chlorides, $\text{mg Cl}^-/\text{L}$	18	28	42	50	25	1000
Total phosphorus, $\text{mg P}/\text{L}$	0.98	1.71	0.68	1.52	0.16	3
Sulphates, $\text{mg SO}_4^{2-}/\text{L}$	41.2	226.4	308.7	679.1	192.1	500
Total dissolved solids, mg/L	400	970	1,500	1,600	985.0	–
Total solids, mg/L	4,200	1,200	10,250	4,600	985.0	
Total suspended solids, mg/L	2,700	363	8,600	2,400	0.00	35
BOD_{5T} , $\text{mg O}_2/\text{L}$	596	134	40	30	–	25
COD_{Cr} , $\text{mg O}_2/\text{L}$	3,980	100	400	125	66.0	125
TOC, $\text{mg C}/\text{L}$	1,492	37	150	46	30.0	30

Table 2
Concentration of heavy and alkaline metals in leachate samples (mg/L)

Parameter	Tests performed in the following years					Acceptable values [13]
	2014–2015				2019	
	Sample No.					
	1	2	3	4	5	
Cu	0.003	0.009	0.011	0.019	0.002	0.5
Cd	<0.001	<0.001	<0.001	<0.001	<0.001	0.4 daily average
Cr^{6+}	–	–	–	–	–	0.1
Total Cr	0.006	0.020	0.363	0.019	0.022	0.5
Ni	<0.004	<0.004	<0.004	<0.004	<0.004	0.5
Zn	0.003	<0.001	<0.001	<0.001	0.006	2.0
Pb	0.005	0.015	0.025	0.048	<0.005	0.5
Mn	0.014	<0.001	<0.001	<0.001	–	–
Fe	0.181	0.047	0.03	0.043	0.089	10.0
Ca	35.37	89.76	197.48	407.53	533.04	–
Mg	3.33	0.06	0.077	0.045	–	–
Hg	–	–	–	–	<0.00002	0.06 daily average

performed by Polish environmental protection services indicated particularly high chromium content in wastewater samples taken from sumps located at the concrete production site. The services recommended the plant owners to perform physicochemical composition tests on the leachates coming from the industrial waste heap. It was stated that the leachates must not be discharged directly to the municipal sewerage system and should be pre-treated at the site. A proposal for the transportation of leachates

in tankers to proper wastewater treatment plant was also submitted [12,16].

Our own research work performed in 2014 and 2015 confirmed the occurrence of irregularities in waste management at that place. The recommendations were partly accomplished. Tests performed for selected leachate parameters in 2019 have shown a significant improvement of the environmental quality compared to the past period. Test results from 2014–2015 and 2019 are put in Tables 1

Table 3
Primary test results statistics

Variable	Sample No 1	Sample No 2	Sample No 3	Sample No 3	Sample No 5
	Average	Minimum	Maximum	Lower quartile	Upper quartile
pH	11.53	7.66	12.80	12.02	12.60
Conductivity, $\mu\text{S}/\text{cm}$	3041	318	6180	1698	4560
Ammonium nitrogen, $\text{mg N-NH}_4^+/\text{L}$	0.216	0.050	0.570	0.080	0.220
Nitrate nitrogen (V), $\text{mg NO}_3^-/\text{L}$	0.162	0.100	0.240	0.100	0.190
Nitrite nitrogen (III), $\text{mg NO}_2^-/\text{L}$	0.005	0.000	0.020	0.000	0.002
Kjeldahl total nitrogen, $\text{mg N}/\text{L}$	2.338	0.640	6.910	0.730	2.510
Chlorides, $\text{mg Cl}^-/\text{L}$	32.6	18.0	50.0	25.0	42.0
Total phosphorus, $\text{mg P}/\text{L}$	1.010	0.160	1.710	0.680	1.520
Sulphates (VI), $\text{mg SO}_4^{2-}/\text{L}$	289.5	41.2	679.1	192.1	308.7
Dissolved matter, mg/L	1,091	400	1,600	970	1,500
Total solids, mg/L	4,247	985	10,250	1,200	4,600
Total suspended solids, mg/L	2,812	0.00	8,600	363	2,700
BOD ₅ , $\text{mg O}_2/\text{L}$	200	30	596	35	365
COD _{Cr} , $\text{mg O}_2/\text{L}$	934	66	3,980	100	400
TOC, $\text{mg C}/\text{L}$	351	30	1,492	37	150

and 2 (samples No 1–4) and as comparative in 2019 (sample No 5). Column 6 indicates the acceptable concentrations in wastewater discharged into the combined sewerage system [13]. It appears from the research work performed during the period of 2014–2015 that in some cases tested leachates contained excessive (exceeding standard values) concentrations of mineral and organic compounds thus limiting a possibility to discharge such wastewater into the domestic or municipal sewerage systems or into waters or ground [13,14]. As it appears from Tables 1 and 2 such excessive values (average daily values) pertained, in accordance with the above-mentioned Regulation, to pH–sample No 3 (12.60), suspended matter–sample No 3 (8,600 mg/L), (BOD - biological oxygen demand) BOD₅–sample No 1 (596 mg O₂/L), (COD - chemical oxygen demand), (COD - chemical oxygen demand) COD_{Cr}–sample No 1 (3,980 mg O₂/L), total organic carbon (TOC)–sample No 1 (1,492 mg C/L), sulphates–sample No 4 (676.1 mg SO₄²⁻/L), calcium–Table 2, sample No 4 (407.53 mg Ca/L) and No 5 (533.04 mg Ca/L). At the same time, the leachates cannot be re-used as the so-called make-up water in concrete production as they show excessive concentrations of some components of given leachate [7,16]. As it appears from the tests performed, leachates from construction materials production flow into the municipal combined sewerage system and accumulate in particular sumps. Due to the occurrence of a relatively high amount of chromium forming non-soluble compounds, this element is accumulated in the form of sediments and is directed, together with municipal wastewater, to the municipal wastewater treatment plant.

4. Statistical analysis of test results for leachates from industrial waste heap

Test results of leachates from technical concrete and construction elements production were subjected to statistical analysis taking into account mutual correlations between

particular components. Table 3 shows primary statistics of leachate test results. Table 4 comprises selected linear correlation coefficients. It was noted that there is a clear positive correlation between chromium, total solids ($r = 0.88$) and suspended matter ($r = 0.93$) (Table 4). Significant values of the coefficient of correlation between BOD₅ and total nitrogen ($r = 0.99$) as well as COD_{Cr} and total nitrogen ($r = 0.91$) were noted. Strong correlations between total suspended matter and chromium ($r = 0.92$) were found; this suggests that chromium compounds are adsorbed mainly by suspended matter particles. A strong correlation between lead compounds and sulphate ions (VI) ($r = 0.96$) indicates a probability of formation of sparingly soluble PbSO₄, whereas the correlation between lead compounds and chlorides ($r = 0.95$) also produces sparingly soluble PbCl₂. For example, the so-called determination coefficient R^2 computed for chromium compounds with total solids and total suspended matter, defines what part of variability of the dependent feature can be explained using the developed model (Table 5). Model results of statistical analysis were illustrated in particular graphs (Figs. 2–4). The correlations shown in those graphs by way of an example illustrate categorized graphs of dispersion together with the regression line. As it appears from those graphs, chromium concentration varies approximately from 0.06 to 0.363 mg Cr/L which partly correlates with the suspended matter indicator from the minute amount to 2,700 mg/L, whereas correlation with the total solids parameter shows, in most cases, values from 985 to 4,600 mg/L. The positive correlation of lead compounds at 0.005 to 0.048 mg/L level and sulphates(VI) from 41.2 to 679.1 mg/L was noted under the same conditions (Fig. 4). Correlation coefficients r between those parameters vary from 0.88 to 0.97.

Table 5 contains primary parameters of statistical assessment including the multiple correlation coefficient, determination coefficient, corrected determination coefficient, F (Fischer) coefficient, critical significance level p , and estimation standard error.

Table 4
Selected coefficients of the multiple correlations

Variable	pH	Cond.	N _{tot}	Cl ⁻	BOD ₅	Pb	Mn	Fe	Cr
pH	1.00	0.69	-0.98	0.63	-0.99	0.45	-0.99	-0.90	0.31
Conductivity	0.69	1.00	-0.78	0.97	-0.82	0.90	-0.71	-0.74	0.38
Ammonium nitrogen	0.02	-0.38	0.11	-0.24	-0.09	-0.23	-0.26	-0.24	0.01
Nitrate nitrogen	0.46	0.37	-0.39	0.52	-0.80	0.53	-0.89	-0.75	0.18
Nitrite nitrogen	0.05	-0.32	0.10	-0.19	-0.11	-0.10	-0.28	-0.22	-0.30
Kjeldahl total nitrogen	-0.98	-0.78	1.00	-0.72	0.99	-0.53	0.95	0.89	-0.39
Chlorides	0.63	0.97	-0.72	1.00	-0.86	0.95	-0.77	-0.77	0.41
Total phosphorus	-0.07	0.12	0.14	0.28	-0.24	0.49	-0.33	-0.23	-0.29
Sulphates	0.59	0.93	-0.65	0.93	-0.75	0.96	-0.67	-0.66	0.06
Dissolved matter	0.82	0.96	-0.88	0.95	-0.93	0.83	-0.86	-0.89	0.49
Total solids	0.04	0.46	-0.17	0.52	-0.27	0.39	-0.15	-0.26	0.88
Total suspended matter	0.04	0.39	-0.16	0.45	-0.25	0.29	-0.15	-0.27	0.92
BOD ₅	-0.99	-0.82	0.99	-0.86	1.00	-0.75	0.98	0.99	-0.43
COD _{Cr}	-0.98	-0.62	0.94	-0.59	0.97	-0.43	0.99	0.91	-0.21
TOC	-0.98	-0.63	0.94	-0.59	0.97	-0.44	0.99	0.91	-0.21

Table 5
Summary of multiple regression

Statistics	Value
Multiple correlation coefficient	0.97
Determination coefficient	0.93
Corrected determination coefficient	0.86
F(2,2)	13.88
p	0.067
Estimation standard error	0.06

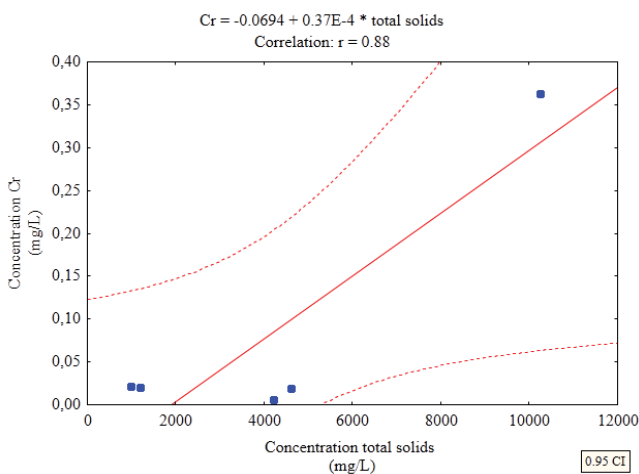


Fig. 2. Categorized graph of dispersion with regression line for total chromium and total solids.

where *F* (*F*-statistic)–statistics of the test verifying the hypothesis that the multiple correlation coefficient significantly differs from 0, which means that at least one parameter of model structural parameters (without free term) differs from

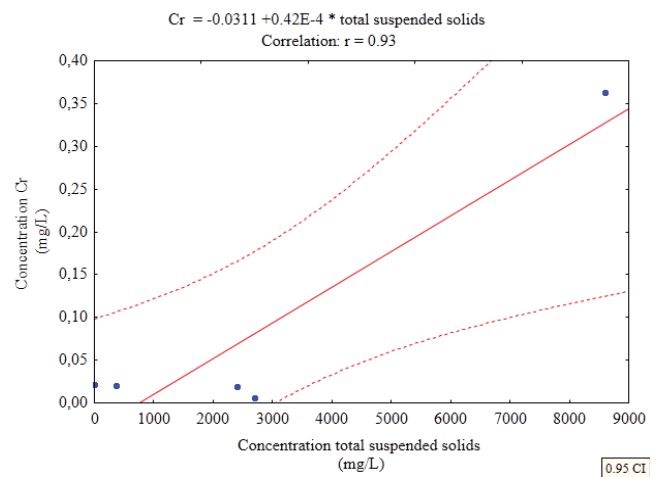


Fig. 3. Categorized graph of dispersion with regression line for total chromium and total suspended matter.

0; *p* (*p*-value)–critical significance level of the test verifying the hypothesis that the multiple correlation coefficient significantly differs from 0.

Performed Fischer *F* test provided significance level at *p* < 0.1, therefore, it requires that at least one coefficient of Eq. (1) β₀, β₁ or β₂ should differ from zero. Estimated values of those coefficients appear to be, in a given case: β₀ = 0.076282, β₁ = -0.000088, β₂ = 0.000137 respectively. Thus, we have two cases when *p* < 0.1. Based on those computations Eq. (1) was formulated as a model describing correlation coefficient values, which can be presented in the following form:

$$Cr = 0.076282 - 0.000088 TS + 0.000137 TSS \tag{1}$$

where Cr–total chromium, TS–total solids, TSS–total suspended solids.

Therefore, one can say that the variables used in the model explain the significant percentage of variability noted for the dependent variable. Putting off any additional dependent variables into the model does not improve definitely particular model parameters. The significance of the model was additionally proved based on an analysis of the correlation between the values determined for Cr and theoretical

values originating from Eq. (1). Confirmation of this conclusion is based on the distribution of reminders nearby the normal distribution (Fig. 5). The results with predicted values and reminders have been set in Table 6. They are used for quick assessment of reminders' quality. As a reminder, the difference between the observed value and that predicted by our model is assumed to be the rest. Observing the rest we could find diverging points if any. Rest values should be as small as possible and comply with the model assumptions when the rest sum equals zero. It appears from Fig. 5 that distribution of rests is equivalent to the normal distribution, which confirms occurrence of strong correlations between particular indicators of pollutants contained in particular leachate samples.

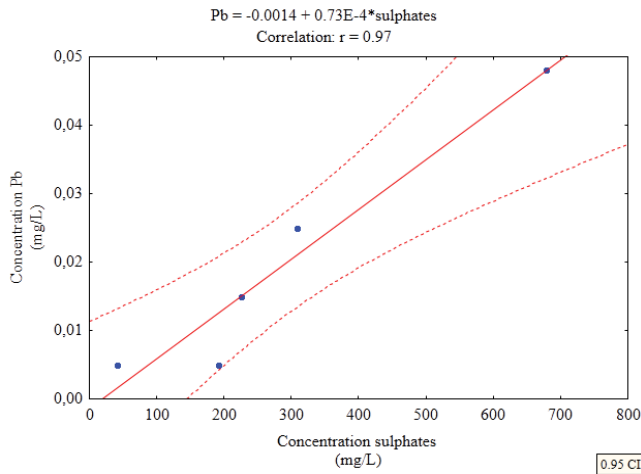


Fig. 4. Categorized graph of dispersion with regression line for total lead and sulphates(VI).

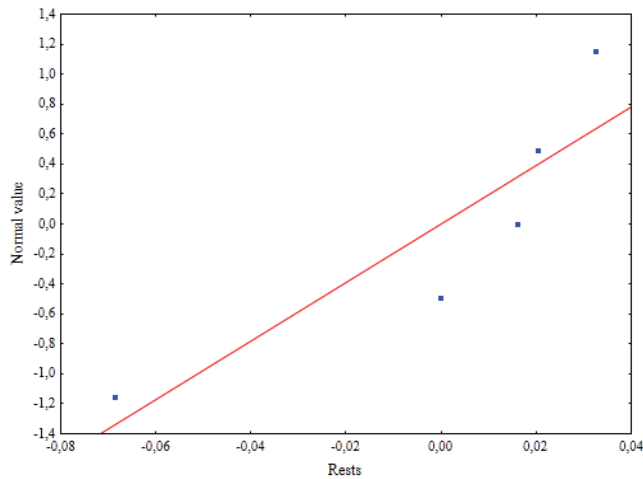


Fig. 5. Distribution of rests nearby the normal distribution.

5. Conclusions

Research work performed at the company confirmed that the highest hazard for the environment (in heavy metals group), as regards leachates from the industrial waste heap, pose compounds of chromium and partly compounds of lead. The highest chromium concentration was noted in leachate samples that created a wastewater pond next to the concrete production unit washing facility (sample No 3). The concentration of total chromium in those leachates amounted to 0.363 mg Cr/L. Chromium Cr⁶⁺ concentration computed for this sample indicates not a very high concentration of this ion being only 0.020 mg Cr/L. This means that the remaining forms of this element were formed with the participation of Cr³⁺ ions. The occurrence of chromium in leachate samples taken from the wastewater pond and sewerage system by the Provincial Inspectorate of Environmental Protection confirmed high chromium concentration in those places. Content of this metal in the sump located nearby the wastewater pond was 31.56 mg Cr/kg DM, whereas in the sediment found nearby the concrete production unit washing facility chromium content was 6.10 mg Cr/kg DM. Control tests performed in 2019, following improvement of the wastewater management at the site, have shown significant improvement of the environmental quality at the concrete elements production plant. On average 0.022 mg/L of total chromium compounds was found in leachates taken to be tested from sumps and piezometric boreholes.

The research performed at the industrial waste heap was an initial stage of work. It consisted of assessment of potential pollution of water and soil at that site. The waste is generated in the production of construction materials when various grades of cement are used. The waste is a source of leachates

Table 6
Results showing predicted values and rests

Observed value	Predicted value	Rest	Standardized predicted forecast value	Standardized rest value	Predicted value standard error
0.006000	0.074769	-0.068769	-0.075036	-1.210260	0.025808
0.020000	0.020087	-0.000087	-0.440367	-0.001536	0.040546
0.363000	0.347111	0.015889	1.744497	0.279634	0.055699
0.019000	-0.001442	0.020442	-0.584203	0.359753	0.053841
0.022000	-0.010525	0.032525	-0.644890	0.572409	0.037079

containing heavy metals, including chromium compounds. The waste was stored directly in sandy and clayish soil without any cover or sealing. The site owners took action aimed at the improvement of the existing environment status, in particular, water supply and sewage disposal. They wish to proceed with the reclamation of the construction materials production site. Our test results indicate a need for continuation of further, detailed soil and leachate testing, including mineral and organic compounds [18]. The sources of this pollution are also their transport facilities responsible for the discharge of petroleum-derived compounds into the ground and aquatic environment. The scope of research should comprise detailed testing of the soil substratum and underground water for the duration of at least one year. Samples of soil, leachates and groundwater should then be taken for testing every month. Similar research works were performed in Poland at former municipal waste landfills. The test results were partly published in an earlier paper and they were: lead (max. 0.15 mg/L), copper (max. 0.032 mg/L), cadmium (max. 0.03 mg/L), chromium (max. 0.04 mg/L), manganese (max. 1.00 mg/L) and zinc (max. 0.41 mg/L) [19]. It can be noted that the concentration of heavy metals, in particular chromium, in leachates from municipals waste landfills was definitely lower than in leachates taken for testing from the heap containing construction industry waste.

The use of statistical analysis for test results processing allowed for finding significant relationships between particular pollutants, which allowed to define the determination coefficient, corrected determination coefficient, F (Fischer) coefficient, critical significance level p and estimation standard error. This allowed for the development of a model describing mutual relationships between leachate components. Particular model variables explain the significant percentage of the dependent variable. The significance of the model was additionally proved based on the analysis of correlations between the values determined for Cr and theoretical values originating from equation (1).

References

- [1] A. Kabata-Pendias, Trace Elements in Soil and Plants, CRC Press, Boca Raton, 2010.
- [2] Z. Kowalski, Z. Wzorek, K. Koneczny, J. Kulczycka, The role of preliminary processing of chromium materials in process of sodium chromate production, *Miner. Resour. Manage.*, 19 (2003) 57–67.
- [3] A. Ešťoková, L. Palaščáková, E. Singovszká, M. Holub, Analysis of the chromium concentrations in cement materials, *Procedia Eng.*, 2 (2012) 123–130.
- [4] L.C. Hills, V. Johansen, Hexavalent Chromium in Cement Manufacturing: Literature Review, Portland Cement Association 2007, R&D Serial No. 2983.
- [5] M. Frias, M.I. Sanchez de Rojas, Total and soluble chromium, nickel and cobalt content in the main materials used in the manufacturing of Spanish commercial cements, *Cem. Concr. Res.*, 32 (2002) 435–440.
- [6] N. Gineys, Influence de la teneur en elements métalliques du clinker sur les propriétés techniques et environnementales du ciment Portland– thèse, Université Lille Nord de France, 2011.
- [7] H. Lu, F. Wei, J. Tang, J.P. Giesy, Leaching of metals from cement under simulated environmental conditions, *J. Environ. Manage.*, 169 (2016) 319–327.
- [8] Z. Guo, M.L. Brusseau, G.E. Fogg, Determining the long-term operational performance of pump and treat the possibility of closure for a large TCE plume, *J. Hazard. Mater.*, 365 (2019) 796–803.
- [9] B. Janowska, K. Szymański, Examples for elimination of selected groups of petroleum-derived compounds from rainwater and meltwater, *Desal. Wat. Treat.*, 52 (2014) 3993–3999.
- [10] Y. Dai, G. Qian, Y. Cao, Y. Chi, Y. Xu, J. Zhou, Q. Liu, Z.P. Xu, S. Qiao, Effective removal and fixation of Cr(VI) from aqueous solution with Friedel's salt, *J. Hazard. Mater.*, 170 (2009) 1086–1092.
- [11] Q.Y. Chen, M. Tyrer, C.D. Hills, X.M. Yang, P. Carey, Immobilisation of heavy metal in cement-based solidification/stabilization, A review, *Waste Manage.*, 29 (2009) 390–403.
- [12] J. Cuevas, A.I. Ruiz, I.S. de Soto, J.R. Procopio, P. Da Silva, M.J. Gismera, M. Regadio, N. Sanchez Jimenez, M. Rodriguez Rastroero, S. Leguey, The performance of natural clay as barrier to the diffusion of municipal solid waste landfill leachates, *J. Environ. Manage.*, 95 (2012) S175–S181.
- [13] Regulation of the Minister of Maritime Economy and Inland Navigation on Substances that are Particularly Harmful for Aquatic Environment and Conditions that must be complied with in Discharging Wastewater into Waters or Grounds as well as in Discharging of Rainwater or Melt Water into Waters, or Water Facilities, Dated 12 July 2019, O.J.L 2019, Section 1311. (in Polish)
- [14] Regulation of the Minister of Housing of 14 July 2006 (Journal of Laws 2006 No 136, item 964). (in Polish)
- [15] I. Del Rey, J. Ayuso, A.P. Galvín, J.R. Jiménez, M. López, M.L. García-Garrido, Analysis of chromium and sulphate origins in construction recycled materials based on leaching test results, *Waste Manage.*, 46 (2015) 278–286.
- [16] G.F. Santonastaso, A. Erto, I. Bortone, S. Chianese, A. Di Nardo, D. Musmarra, Experimental and simulation study of the restoration of a thallium (I) - contaminated aquifer by permeable adsorptive barriers (PABs) (2018), *Sci. Total Environ.*, 630 (2019) 62–71.
- [17] A. Stanis, An Affordable Statistic Course Based on the STATISTICA PL Program on Examples of Medicine, StatSoft Polska Poland, Krakow, 2001. (in Polish)
- [18] I. Bortone, S. Chianese, A. Erto, A. Di Nardo, C. De Crescenzo, D. Karatza G.F. Santonastaso, D. Musmarra, An optimized configuration of adsorptive wells for the remediation of an aquifer contaminated by multiple aromatic hydrocarbon pollutants, *Sci. Total Environ.*, 696 (2019) art no. 133731.
- [19] K. Szymański, I. Siebielska, B. Janowska, R. Sidełko, Variations in physical and chemical parameters of landfill leachates over time, *Desal. Wat. Treat.*, 117 (2018) 149–155.