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HEAVY METALS AND SULFATE REMOVAL FROM WATER BY MEANS OF Al POWDER-CEMENT-BASED FILTRATION

Al powder-cement-based filters used to treat contaminated water from a coal mining area were designed and tested. Several of these multicomponent filters, containing quartz sand, Portland cement and water, as well as additional components (Al powder, CaO and CaSO₄) in various mass proportions have been prepared. In this respect, an exhaustive analysis of the impact of the individual components on the properties of the filters was conducted to evaluate their efficiency in the removal of heavy metals and SO_4^{2-}. Moreover, additional filter properties such as water permeability, uniaxial compressive strength and resistance to frost were also considered. The information gathered revealed that the designed filters pose high efficiency in respect of heavy metal removal (Cu, Cr, Ni, Co, Zn) and also exhibit proper water permeability and high mechanical strength. Based on this analysis, an optimal filter composition is provided. The results reported herein suggest that Al powder-cement-based filters are environmentally sustainable and cost effective for the treatment of water from industrial sites even in cold weather conditions.

1. INTRODUCTION

The building development of urban and industrial areas consisting of single or multi-storey structures as well as concrete or asphalt roads and squares have a negative impact on the natural circulation of water in the natural environment due to the elimination of natural water infiltration processes and limited evaporation. Additionally, the industrial operation of plants, road transport, the operation of fuel stations, emissions to atmospheric air etc. are activities that cause these surfaces to contain large amounts of contaminants such as hydrocarbons and heavy metals, thus posing a significant threat to the natural environment.

The chemical composition of the precipitation water drained from industrial and urban areas as well as their physical and chemical properties are dependent upon: a) the

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mode of land development and usage, b) the type of the materials used for the construction of roofs and other structures exposed to atmospheric precipitation, c) the type of the drained surface and the snow removal method, d) the type of liquid and solid substances used in the industrial plant, e) the emission of gases and dusts to atmospheric air, f) the intensity and duration of rain and the duration between subsequent rainfalls.

In the recent years, a lot of attention has been devoted to oil pollutions in precipitation water (rain and snow wastewater), which was supported by an increasingly rich market offer and marketing activities taken up by manufacturers of separators. A typical rainwater sewage treatment plant, encompassing a settling tank and an oil separator, often integrated into a single unit, does not, however, solve the problem of risks related to rainwater drained from urban areas. An increasing number of studies [1, 2] indicates also the presence of other contaminants in the rain sewage water (heavy metals, chlorides, sulfates, biogenic compounds, microorganisms) exhibiting adverse effects on the soil environment and water bodies and thus also on the living organisms. Table 1 presents the concentrations of metal and sulfate ions in precipitation water drained from the area of a Polish coal mine. Supplementing the devices used for the treatment of rainwater and snowmelt by an additional stage for removing the excessive amounts of dissolved metals and sulfates would allow for the protection of surface waters.

Table 1

Properties of the precipitation water

Parameter	Value
pH	6.24
Dissolved oxygen, mg/dm^3	9.09
Temperature, °C	6.0
Suspended solids, mg/dm^3	6174
Cr^{6+}, mg/dm^3	0.098
Cu, mg/dm^3	0.49
Ni, mg/dm^3	0.243
Co^{2+}, mg/dm^3	0.317
Pb, mg/dm^3	0.247
Cd, mg/dm^3	0.031
Zn^{2+}, mg/dm^3	1.21
Fe_{total}, mg/dm^3	1.79
SO_4^{2-}, mg/dm^3	187
Cl^-, mg/dm^3	150
The mean yield of rainwater flowing into the receiver, dm^3/min	36

Keeping in mind that there are many works confirming the observation regarding the high concentrations of metals dissolved in water [3, 4, 2] and taking into account the current dense development, increasing traffic and air pollution, one should consider

whether rainwater sewage should not be subject to broader legal regulations. In line with the Ordinance of the Minister of Environment dated November 18th, 2014 [5], the requirements regarding rainwater and snowmelt sewage drained by sewage systems and originating mostly from impenetrable surfaces only provide for the allowable content of total suspended solids (100 mg/dm^3) and petroleum hydrocarbons (15 mg/dm^3) in wastewater introduced to water bodies or soil.

To purify water with a high content of metal ions and SO_4^{2-} as well as low pH values, various passive methods may be used, such as anoxic limestone drains, aerobic wetlands, compost reactors/wetlands, packed bed iron-oxidation bioreactors [6], anaerobic sulfate-reducing bioreactors, constructed wetlands [7] and WTRs-based filter media [8]. Most of them are costly, require constant maintenance, and cannot address the problems with low pHs and high concentration of metal ions over a prolonged period of time [7]. Hence, there is an urgent need to develop technically and economically effective water treatment methods.

The aim of the authors was to create a filter that would allow for an efficient, long-lasting and stable operation consisting in the removal of contaminants dissolved in rainwater transported to surface waters by means of rainwater sewage systems. The basic characters of such filters include reactivity (capability to remove contaminants), long-lasting water permeability and compressive strength including changes in strength resulting from frost with consideration given to the NaCl solution present in water in the period of snow removal from industrial areas, roads and other paved surfaces.

2. MATERIALS AND METHODS

Two series of studies were conducted. The first one was the selection of a suitable dose of Portland cement to optimize the compressive strength without significant loss of permeability of the filters, as well as of an adequate content of aluminum powder to optimize the hydraulic conductivity without remarkable loss of mechanical strength of the filters. Six samples (F1–F6) were prepared in the second stage. The samples contained similar amounts of aluminum and Portland cement but differed in the contents of metallic iron and calcium carbonate. The ability of the filters has been evaluated in terms of removal of heavy metals and sulfates from water depending on the content of additional components. Then their impact on the permeability of water and strength of the filters, including their resistance to frost (including the presence of NaCl solution) has been evaluated.

Materials. The filters for the removal of metal ions have been made from materials forming a water-permeable structure such as quartz sand, 42.5 Portland cement, calcium oxide, precipitated calcium carbonate, metallic iron (powder), anhydrous calcium sulfate; aluminum powder and water. Detailed characteristics of calcium oxide, metallic

iron, calcium carbonate and aluminum powder are given in Table 2, the basic parameters of the materials used in the production of the filters – in Table 3. Mass fractions of iron and calcium carbonate in particular filters ranged from 0 to 5 wt. %. The granular compositions of the materials used have been determined using a particle size analyzer and presented in Table 3. Their values indicate very fine or fine grain sizes of the applied materials. Finer grains mean shorter reaction times during the production of filters, the processes occurring more smoothly, and the higher filter stability. Table 3 also presents the results of the bulk density analysis for the condensed state and the results of the analysis of water used in the production of filters.

Table 2

Specification of components used in the production of filters[a]

Property	CaO (96–100.5%)	Fe(0) ($\geq$99%)	CaCO$_3$ ($\geq$98.5%)	CaSO$_4$	Al (99%)
Character	powder (fine)	powder (fine)	white powder	white granules grain size 2.38 mm	silver-gray powder
Impurities [wt. %]	$\leq$0.5 insoluble in HCl $\leq$2.5 Mg	$\leq$0.5 insoluble in HCl	$\leq$0.02 insoluble in HCl	nda	nda
Boiling point [°C]	2850	2750	nda	nda	2467
Melting point [°C]	NDA	1535 °C	NDA	1450	660
Anion traces	F$^-$ $\leq$ 150 mg/kg	Cl$^-$ $\leq$ 20 S^{2-} $\leq$100 mg/kg	Cl$^-$ $\leq$ 0.01 SO$_4^{2-}$ $\leq$ 0.1 wt. %	nda	nda
Cation traces	As $\leq$3 Pb $\leq$2 mg/kg	As $\leq$ 5 Cu $\leq$ 100 Mn $\leq$ 1000 Ni $\leq$ 500 Pb $\leq$ 20 Zn $\leq$ 50 mg/kg	As $\leq$ 0.0005 Ba $\leq$ 0.01 Cu $\leq$ 0.001 Pb $\leq$ 0.002 K $\leq$ 0.05 Na $\leq$ 0.1 Fe $\leq$ 0.003 wt. %	nda	nda
Others	$\leq$3.5 wt. % loss in ignition	resistivity 9.71 μΩ·cm	molar mass 100.09 g/mol	solubility in water at 20 °C 2.4 g/dm^3	insoluble in water and organic solvents, no smell

[a]In line with the producers' catalogues: www.poch.com.pl; www.sigmaaldrich.com, nda – no data available.

Filter production method. The filters for the removal of metal ions from water have been prepared (Fig. 1) based on the work [9]. The composition of the filters used is

given in Table 4. First, adequate masses of quartz sand, metallic iron and calcium carbonate have been mixed together. In the first stage of the research and in the filter F1 of the second stage, the filters only comprised of quartz sand.

Parameters of materials used in the production of filters

Parameter	Quartz sand	CaCO$_3$	Fe(0)	Cement (42,5)	CaO	Water	Al	CaSO$_4$
Specific density, g/cm^3	2.58 18 °C	2.93 20 °C	7.86 25 °C	3.01 18 °C	3.30 25 °C	0.998	2.66 at 18 °C	2.72 at 18 °C
Size (μm) distribution	400–300 25% 300–200 52% 200–100 23%	120–80 14% 80–50 32% 50–30 24% 30–5 30%	80–60 5% 60–40 36% 40–20 41% 20–5 18%	140–70 6% 70–40 26% 40–20 41% 20–5 27%	100–80 15% 80–50 41% 50–10 30% 10–5 14%	–	70–50 41% 50–30 48% 30–15 11%	120–100 24% 100–70 34% 70–50 26% 50–30 16%
Bulk density[a] g/cm^3	1.68	0.91	2.24	1.51	1.45	–	1.34	1.29
Others	SiO$_2$ > 90%							solubility in water 2.4 g/dm^3 at 20 °C
Data for water: pH = 7.21, TDS 750 mg/dm^3, conductivity 1.17 mS/cm, carbonate hardness 290 mg/dm^3 CaCO$_3$								

[a]In the concentrated state.

In the second stage, the F2 and F6 filters comprised only of quartz sand and calcium carbonate and of quartz sand and metallic iron, respectively. F3, F4 and F5 filters contained also additives of calcium carbonate and metallic iron in varying proportions. Such mixtures were supplemented with anhydrous calcium sulfate and 70 wt. % of the amount of water specified in Table 4. Subsequently, Portland cement, the remaining amount of water at 10 °C as well as burnt lime were added. In the end, aluminum powder was added (with caution, the reaction generates flammable gases) and all ingredients were mixed using an ML-11 laboratory mixer. The resulting mixtures were introduced to greased forms (geometric parameters of forms/columns differed depending on the study), in which the bonding reactions of the filter proceeded, thus creating a stable solid body. The mixture samples for the determination of strength parameters were introduced to metal cylindrical forms in line with PN-G/11011 with dimensions of 80 mm in diameter and 80 mm high. The samples for the determination of the hydraulic conductivity, bulk density and porosity were introduced to plastic forms 100 mm in diameter and 50 mm high. The fluid mass was poured to the half of the forms' volume, as for an hour its volume increased twice. The temperature distinctly increased during these processes.
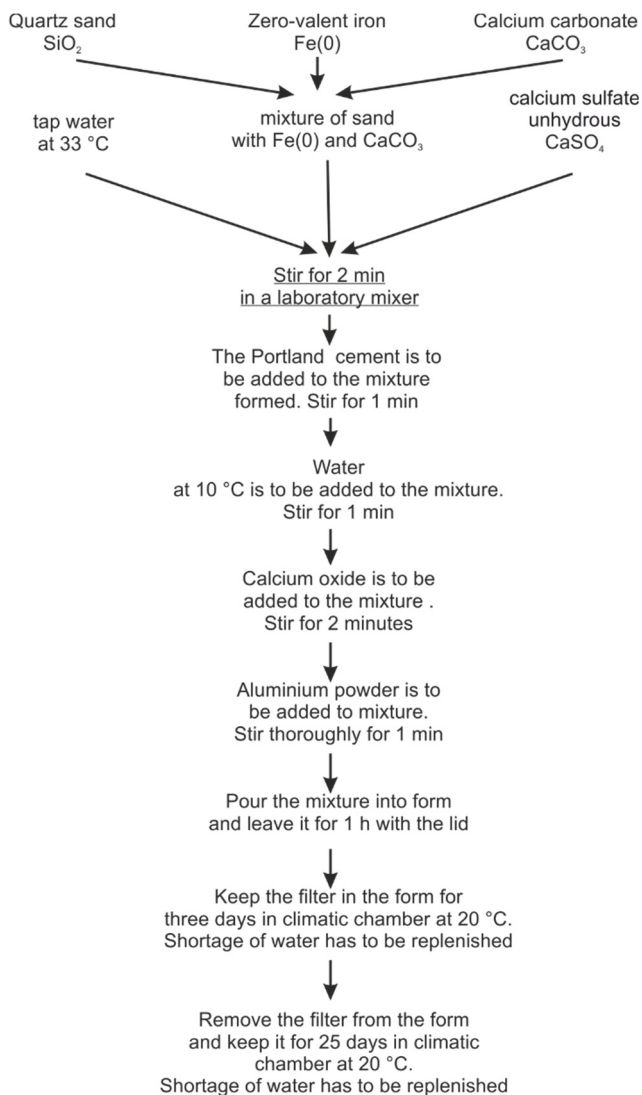
Quartz sand
SiO_2

Zero-valent iron
Fe(0)

Calcium carbonate
$CaCO_3$

tap water
at 33 °C

mixture of sand
with Fe(0) and $CaCO_3$

calcium sulfate
unhydrous
$CaSO_4$

Stir for 2 min
in a laboratory mixer

The Portland cement is to
be added to the mixture
formed. Stir for 1 min

Water
at 10 °C is to be added to the mixture.
Stir for 1 min

Calcium oxide is to be
added to the mixture .
Stir for 2 minutes

Aluminium powder is to
be added to mixture.
Stir thoroughly for 1 min

Pour the mixture into form
and leave it for 1 h with the lid

Keep the filter in the form for
three days in climatic chamber at 20 °C.
Shortage of water has to be replenished

Remove the filter from the form
and keep it for 25 days in climatic
chamber at 20 °C.
Shortage of water has to be replenished

Fig. 1. The modified method of preparing filters for the removal
of metal ions from water (based on [9])

The filters were left in the forms for three days with sufficient amount of water until setting and achieving the minimal strength. Then the samples were taken out from the cut forms and seasoned for 28 days in a climatic chamber manufactured by Elbanton; adequate amount of water was provided throughout the entire seasoning. The composition of filters based on Al powder and cement, as well as the method of production have been patented [10].

Composition and physical parameters of filters used for the removal of metal ions from rainwater

M	Al powder content [%]					Portland cement content [%]				Filter					
	0.7	0.5	0.3	0.2	0.1	25	20	15	10	F1	F2	F3	F4	F5	F6
1	44.5	44.7	44.9	45.0	45.1	35	40	45	50	45	40	40	40	40	40
2	0	0	0	0	0	0	0	0	0	0	5	3.5	2.5	1.5	0
3	0	0	0	0	0	0	0	0	0	0	0	1.5	2.5	3.5	5
4	15	15	15	15	15	25	20	15	10	15	15	15	15	15	15
5	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
6	28	28	28	28	28	28	28	28	28	28	28	28	28	28	28
7	0.7	0.5	0.3	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Parameters (P)															
9	2.54	2.54	2.53	2.53	2.53	2.54	2.53	2.53	2.50	2.53	2.55	2.56	2.56	2.58	2.60
10	0.831	0.844	0.807	0.820	0.891	0.924	0.881	0.820	0.829	0.820	0.871	0.891	0.925	0.947	0.981
11	5.47	6.47	8.27	5.11	0.881	4.21	4.56	5.11	5.20	5.11	4.29	4.47	5.49	5.39	5.91
12	0.3275	0.3479	0.3415	0.3355	0.2486	0.2914	0.3057	0.3355	0.3512	0.3355	0.2721	0.2894	0.2991	0.3084	0.3110
13	0.51	0.54	0.61	0.43	0.64	0.91	0.74	0.43	0.11	0.43	0.51	0.71	0.73	0.71	0.79
14	0.46	0.47	0.50	0.31	0.42	0.82	0.53	0.31	0.09	0.31	0.44	0.61	0.54	0.61	0.77
15	0.39	0.44	0.41	0.28	0.28	0.70	0.39	0.28	0.06	0.28	0.32	0.45	0.35	0.41	0.66
16	9.8	13.0	18.0	27.9	34.4	9.9	28.4	27.9	18.2	27.9	13.7	14.1	26.8	14.1	2.5
17	23.5	18.5	32.7	34.9	56.25	23.1	47.3	34.9	45.5	34.9	37.3	36.6	52.1	42.3	16.5

M – material, 1 – quartz sand, 2 – calcium carbonate, 3 – zero valent iron, 4 – portland cement, 5 – calcium oxide, 6 – water, 7 – aluminum powder, 8 – anhydrous calcium sulfate, 9 – specific density at 20 °C, g/cm^3, 10 – bulk density of the filter, g/cm^3, 11 – hydraulic conductivity, 10^{-4} m/s, 12 – effective porosity, 13 – R_1, mean compressive strength of the control samples, MPa, 14 – R_2, mean compressive strength of samples frozen and saturated with distilled water, MPa, 15 – R_3, mean compressive strength of samples frozen and saturated with NaCl solution, MPa, 16 – ΔR_I, mean loss of strength of the samples for the samples only subject to freezing, %, 17 – ΔR_{II}, mean loss of strength of the samples for the samples subject to freezing and the action of NaCl, %.

Research method. The parameters of the applied components and the filters themselves (Tables 3, 4) have been specified using the following methods:

• Pycnometer method in line with the PN-88/B-04481 standard for the determination of specific density of the used components and the produced filter. The specific density was measured after crushing and size reduction.

• Laboratory method using the so-called Wiłun apparatus for the determination of the hydraulic conductivity. The filters were paraffin-sealed in the apparatus.

• Method of high columns for the determination of effective porosity. The parameter is defined as the ratio of the active porous space volume during filtration and the total volume of the rock. The parameter, with certain deviations, may be equal to the

storage coefficient. Thus, while measuring the storage coefficient, one obtains an approximated value of the effective porosity of the filters. In the case of cement-based samples which absorb large amounts of water in the dry-state, the analyses were conducted for moist material. The preparation of filter samples consisted of placing them in a cell with water for 5 min and subsequent removing the excess water with a vacuum pump set at a pressure of 6.864×10^4 Pa. The process of the removal of water from the filters (gravitational water from pores) lasted 15 min. The samples were then subjected to analysis to determine the effective porosity.

• Method for the measurement of single-axis compressive strength (R_c) using a EU40 strength testing machine. The analysis has been conducted in the following way (testing lasted 5 days): one sample (control sample) was saturated with water only and was left at 18 °C for the entire time of testing the resistance to frost and chemical agents. The remaining two identical samples were introduced to a freezer. For 4 h, the samples were subject to cyclic freezing (25 repetitions) and unfreezing (at 18 °C) by absolute immersion, both of the second and third sample in distilled water and in a 3 wt. % solution of NaCl, respectively. After the final unfreezing, the strength test was performed both for the control sample and the sample that was subjected to freezing as well as the sample that was subjected to both freezing and chemical agents. The mean loss of strength of the samples has been calculated using the following equations:

• For the samples subject only to freezing

$$\Delta R_{\mathrm{I}} = \frac{R_1 - R_2}{R_1} \times 100\% \tag{1}$$

• For the samples subject to freezing and the action of NaCl

$$\Delta R_{\mathrm{II}} = \frac{R_1 - R_3}{R_1} \times 100\% \tag{2}$$

where R_1 – mean compressive strength of the control samples – not frozen, water saturated, MPa, R_2 – mean compressive strength of samples (after the last unfreezing) that were frozen and saturated with distilled water, MPa, R_3 – mean compressive strength of samples (after the last unfreezing) that were frozen and saturated with 3 wt. % NaCl solution, MPa.

To determine the efficiency of the filters in the removal of heavy metals from water depending on the content of constituents, two series of studies were performed. The first series was conducted with the use of distilled water as the medium flowing through the filters. This study was to specify their background, that is the type of metals and other compounds released to the flowing water. The second series of studies has been performed using distilled water contaminated with heavy metals, so as to achieve a solution

corresponding to the rainwater flowing from the area of the coal mine in terms of composition as well as physicochemical parameters (Table 1). The solution for testing has been prepared in the laboratory by adding adequate amounts of p.a. purity chemical agents to 20 dm^3 of distilled water (ZnSO$_4\times$7H$_2$O, NiSO$_4\times$7H$_2$O, CoCl$_2$, CuSO$_4\times$5H$_2$O, NaCl, K$_2$Cr$_2$O$_7$, H$_2$SO$_4$). To the pH of the solution to slightly acidic, approximately 100 cm^3 of 1 M NaOH was added.
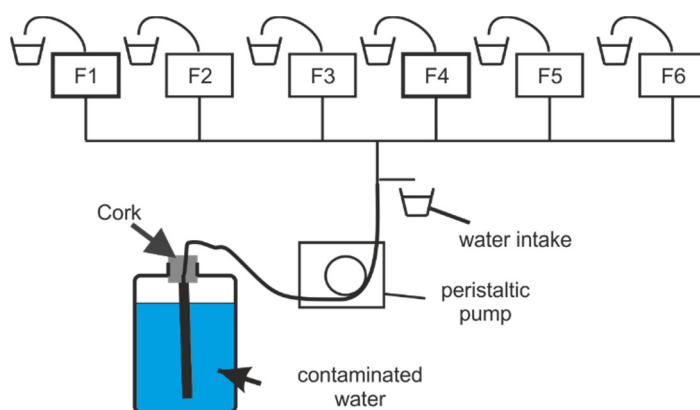
Fig. 2. Test stand for the simulation of flow and purification
of contaminated water using filters

The analyses were conducted using a laboratory stand presented in Fig. 2. The prepared solution was transferred through six filters in differing in composition placed in Teflon columns. 635 g of the mixture was poured into each of the columns and left for 28 days until set. The diameter and the height of the filters were 90 mm and 100 mm, respectively. A ZALIMP PP1B-05A peristaltic pump pumped water from the bottom to the top of the columns with a 40 cm^3/min rate (per each filter separately), which resulted in the water being retained in the filter for approximately 16 min. The mean flow rate of precipitation water drained through sewage system in the sampling point amounted to 36 dm^3/min (Table 1). To obtain similar efficiency and the 16 min time of water retention in the filter, the height of a filter 1 m in diameter would be 0.71 m.

Water used in the analysis of the physicochemical parameters and the concentrations of selected metals were sampled at the inlet of the system and at the outlet of the columns (Fig. 2). To determine the treatment stability, the analyses were conducted continuously for a period of two weeks while studying the analyzed parameters and concentrations every 4 days. The tests results are presented in Tables 5 and 6.

Temperature, pH, the redox potential and the electrolytic conductivity have been determined using electrometric methods (using Knick PORTAMESS meters. Also, the following parameters were determined for the water:

• The concentrations of Cr^{6+}, Fe^{2+}, Fe_{tot}, (Fe^{3+} as a difference in Fe_{tot} and Fe^{2+}), Cu_{tot}, Ni_{tot}, Co_{tot}, Zn_{tot}, Mn_{tot}, Al^{3+}, SO_4^{2-}, Cl^-. The analyses were made using the HachLange UV-Vis DR5000 spectrophotometer by the powder methods.

• The hardness in line with the PN-ISO 6059:1999.

First, the measurements were made using PORTAMESS meters. Then the concentrations of Fe^{2+} ions was determined to prevent their oxidation to Fe^{3+}. The sequence of the remaining determinations was random. All the analyses were conducted at 19–20 °C.

3. RESULTS AND DISCUSSION

For water purification, metal compounds were precipitated by increasing pH of the solutions. Metallic iron, known as an efficient material for the reduction as well as precipitation and adsorption of heavy metals [11], together with calcium carbonate, acting as possible pH buffer protecting against aggressive chemical substances such as sulfuric and hydrochloric acids were used as a support for that process.
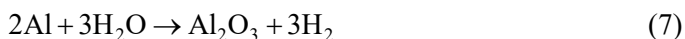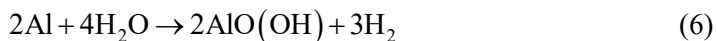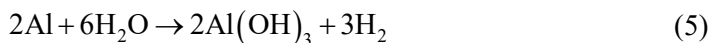
To obtain high permeability of the filters, fine-grained materials such as aluminum powder were used, which allowed the increase in their effective porosity and the hydraulic conductivity and to decrease the bulk density. Since many years, the aerated autoclaved concrete (AAC) characterized by similar parameters has been used in residential buildings. The addition of aluminum powder allowed the formation of a porous structure, as in its reaction with the hydroxides derived from cement (reactions (12), (13)) and in the slaking of burnt lime

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{3}$$
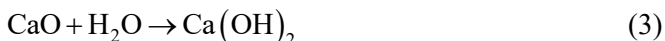
Hydrogen was produced, in line with the following reaction:

$$2Al + 3Ca(OH)_2 + 6H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + 3H_2 \tag{4}$$

which caused the formation of pores in the setting mixture and the increase in its volume by nearly 2 orders of magnitude. According to the authors of the work [12], the formation of hydrogen may also result from the reaction of aluminum and water:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \tag{5}$$

$$2Al + 4H_2O \rightarrow 2AlO(OH) + 3H_2 \tag{6}$$
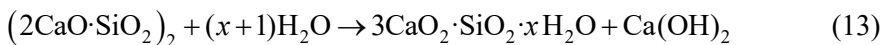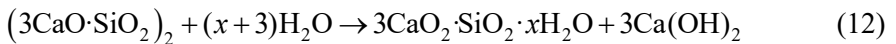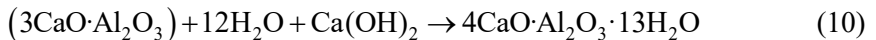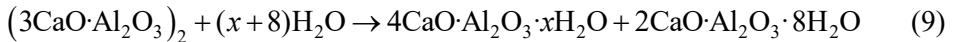
$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 \tag{7}$$

As the reactions (4)–(7) are strongly exothermic, the temperature of the mixture increased.

Calcium oxide was the source of $CaCO_3$, which is considered one of the main bonding agents. The formation of calcium carbonate from $Ca(OH)_2$ – the product of reactions (3), (12) and (13), as well as from CO_2 dissolved in water, is described by the following reaction:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{8}$$
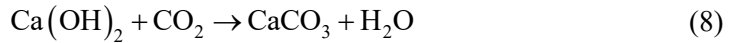
Calcium also delivers heat to the produced mixture, as the described reactions in which it participates are strongly exothermic. Without that constituent, the formation of gas would be limited and the rigidity of the structure would be significantly lower.

Portland cement obtained by grinding cement clinker and up to 5 wt. % of gypsum undergoes crystallization in the bonding process, thus forming a rigid and hard mass. The cement consists of a mixture of silicates and oxides such as $2CaO \cdot SiO_2$ – belite, $3CaO \cdot SiO_2$ – alite, $3CaO \cdot Al_2O_3$) – celite, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ – brownmillerite. The bonding process itself consists in chemical reactions, the most important of which are [13]:

$$(3CaO \cdot Al_2O_3)_2 + (x+8)H_2O \rightarrow 4CaO \cdot Al_2O_3 \cdot xH_2O + 2CaO \cdot Al_2O_3 \cdot 8H_2O \tag{9}$$

$$(3CaO \cdot Al_2O_3) + 12H_2O + Ca(OH)_2 \rightarrow 4CaO \cdot Al_2O_3 \cdot 13H_2O \tag{10}$$

$$(4CaO \cdot Al_2O_3 \cdot Fe_2O_3) + 7H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + CaO \cdot Fe_2O_3 \cdot H_2O \tag{11}$$

$$(3CaO \cdot SiO_2)_2 + (x+3)H_2O \rightarrow 3CaO_2 \cdot SiO_2 \cdot xH_2O + 3Ca(OH)_2 \tag{12}$$

$$(2CaO \cdot SiO_2)_2 + (x+1)H_2O \rightarrow 3CaO_2 \cdot SiO_2 \cdot xH_2O + Ca(OH)_2 \tag{13}$$

The sand used in the study contained over 90 wt. % of crystalline silicon, mostly SiO_2 quartz with a grain size from 0.1 to 0.4 mm (Table 3). The amount of that mineral should be at least 85 wt. % [9]. Fine grains of sand which decrease the time of production, the crystallization level and increase the compressive strength have been used in the production of the filter. These properties are fundamental for the production of stable filters which may be used multiple times. Cement and calcium oxide were also necessary to produce strongly basic and reductive conditions in the flowing water, which are the fundamental factors in the removal of metal ions.

Anhydrous $CaSO_4$ was added during the production of filters to increase their compressive strength and to avoid the collapsing of the mixture [9]. In order to obtain granular composition allowing the reduction of the reaction time, the compound was ground to the level

presented in Table 3. The content of water resulted in a proper course of the bonding process, while its amount had a significant impact on the strength parameters of filters.

3.1. EFFECT OF THE PORTLAND CEMENT CONTENT ON THE FILTER PROPERTIES

Due to the necessity to transport and regenerate the filters, their single-axis compressive strength and their resistance to low temperatures and chemical agents (NaCl salts used in snow removal) are the basic qualities of the filters. Considering that the filters are characterized by high porosity and they are not intended as a structural element, based on experiments it may be assumed that the target compressive strength (following the frost resistance tests including the action of NaCl solution on the samples and soaking) should not be lower than 0.2 MPa.

A filter that would allow for a long-term and stable operation consisting in the removal of contaminants dissolved in precipitation water should also be characterized by high hydraulic conductivity. It is assumed that the filters for the treatment of precipitation water should be characterized by water permeability similar to that of coarse-grain sands being in the range between $5 \cdot 10^{-4}$ m/s and $1 \cdot 10^{-3}$ m/s [14].

An increase in the content of Portland cement in the filter composition to improve their compressive strength has insignificantly lowered their effective porosity and the hydraulic conductivity of the samples, thus increasing their bulk density (Table 4). A higher amount of cement also causes an increase in the cost of filter production and may decrease their reactivity with regards to heavy metals. However, it may be said with all certainty that along with the increase of the cement amount, the compressive strength of the samples increases. This also concerns the resistance to low temperatures and chemical agents (NaCl solution). The increase in strength between its 15% and 25% contents is not high enough to substantiate the use of larger amounts of Portland cement in the production of filters. The expected value of compressive strength, that is 0.2 MPa, is achieved in the case of the filter with a 15% cement content. A lower part of cement, amounting to 10 wt. % causes the mean single-axis compressive strength of the samples to decrease even to the value of 0.06 MPa in case of samples that were frozen and saturated with 3 wt. % NaCl solution. Due to the above, the part of Portland cement in further research amounted to 15 wt. %.

3.2. EFFECT OF THE ALUMINUM POWDER CONTENT ON THE FILTER PROPERTIES

The increase of the aluminum powder content in the filter composition from 0.2 to 0.7 wt. % did not cause significant changes in the bulk density of filters, their effective porosity or the hydraulic conductivity (Table 4). The changes in these parameters are more influenced by the method of sample preparation or by the methods of measurements rather than by the increase of the aluminum powder content. Due to the above, it may be stated that a higher part of the aluminum powder does not cause any increase in

the water permeability and – what is significant – does not cause a decrease in the R_c resistance below the assumed value. Thus, there are no grounds to use amounts of aluminum powder exceeding 0.2 wt. % in the production of filters.

Decreasing the content of the aluminum powder to 0.1 wt. %, however, causes remarkable changes in the analyzed parameters. The hydraulic conductivity and the effective porosity values are then lowered to 8.81×10^{-5} m/s and 0.2486, respectively, while the bulk density slightly increases to 0.891 g/cm^3. Noting especially the hydraulic conductivity being below the assumed value, it has been concluded that the mass content of the aluminum powder should be 0.2 wt. %.

3.3. RESULTS OF FILTER EFFICIENCY TESTS

The background of the filters was mostly related to their structure and – to a lesser extent – to the conditions in which the filters were used. Table 5 presents the changes in the physicochemical parameters and the content of substances observed in distilled water before and after flowing through the filters. Among the physicochemical parameters, the greatest changes were noted in pH values, specific electrolytic conductivity and the redox potential. The pH values increased from 7.30 to nearly 12.5, the electrolytic conductivity increased from $1.8 \cdot 10^{-3}$ mS/cm to over 7.5 mS/cm and the redox potential values decreased from 121 mV to less than –110 mV. This provided evidence that after flowing through the filters, the water exhibited strongly reductive, basic properties and a very high electrolytic conductivity value resulting from the fact that mostly hydroxides, bicarbonates, carbonates and – to a lesser extent – magnesium are released to water. Based upon the Eh-pH diagrams presented in the work [15], it has been concluded that these conditions are favourable for the formation of precipitated metal forms: Cu, Cr, Fe and/or the formation of metals in anionic form: Ni, Cu, Zn. In the diagrams the metals (Me) are analyzed in Me–O–H systems.

High contents of hydroxides, bicarbonates, and calcium carbonates expressed in Table 5 as temporary, total and calcium hardness indicate very hard water. The increase of these values and the specified physicochemical parameters is related to the material used for the production of filters. Although this aspect may not be eliminated, it may be reduced by ensuring an adequately long time of hydration. In the view of the authors, the analyses using the filters have been conducted too soon from their preparation. This may be evidenced by high pH and hardness values.

Irrespective of the above, it should be noted that the impact of water hardness on the natural environment and the living organisms is relatively small and of no sanitary or health significance. To the contrary, the increased content of magnesium and calcium contributing to the hardness is favorable e.g. in terms of water intended for consumption. This is why the hydroxides and calcium and magnesium bicarbonates released to the water environment are not detrimental to the natural environment and living organisms. It should be also added that the pH value and the redox potential of the treated

water reaching the water body (river, underground water) will return to its normal, neu-
tral condition after dilution or they can be regulated by using neutralizing reagents.

Filter backgrounds. Values of the physicochemical parameters and the content
of chemical substances observed in distilled water before and after flowing through the filters

Parameter	Distilled water	Water after flowing through the filter					
		Filter					
		F1	F2	F3	F4	F5	F6
pH	7.30	12.68	12.66	12.68	12.73	12.71	12.67
Conductivity, mS/cm	$1.8 \cdot 10^{-3}$	7.78	7.56	7.91	8.10	8.24	8.52
Redox potential, mV	121	−115	−116	−121	−110	−122	−117
Temperature, °C	19.6	19.8	19.3	19.8	19.5	19.3	19.5
Temporary hardness, mg $CaCO_3/dm^3$	<5	660.56	715.89	628.97	660.56	700.89	711.60
Total hardness, mg $CaCO_3/dm^3$	<5	720.70	765.15	710.53	697.32	749.80	754.62
Calcium hardness, mg/dm^3 Ca as $CaCO_3$	<5	680.55	704.82	645.74	675.91	700.89	736.59
Fe^{2+}, mg/dm^3	<0.02	0.08	0.07	0.28	0.24	0.21	0.30
Fe_{tot}, mg/dm^3	<0.02	0.09	0.09	0.34	0.21	0.31	0.30
Fe^{3+}, mg/dm^3	–	0.01	0.02	0.06	–	0.10	0.00
Cu_{tot}, mg/dm^3	<0.04	<0.04	<0.04	<0.04	0.05	<0.04	<0.04
Cr^{6+}, mg/dm^3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni_{tot}, mg/dm^3	<0.006	<0.006	<0.006	<0.006	<0.006	0.021	<0.006
Co_{tot}, mg/dm^3	<0.006	<0,006	<0.006	<0.006	<0.006	0.014	<0.006
Zn_{tot}, mg/dm^3	<0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01
Mn_{tot}, mg/dm^3	<0.007	0.071	0.076	0.174	0.201	0.184	0.121
Al^{3+}, mg/dm^3	<0.008	0.022	0.041	0.012	0.042	0.029	0.009
SO_4^{2-}, mg/dm^3	<2	<2	<2	<2	<2	<2	<2
Cl^-, mg/dm^3	<5	9.75	19.53	20.17	23.08	22.00	24.85

The increased content of Al^{3+} observed in water after passing through the filters
(Table 5) also results from the material they have been made of. These concentrations
are very low. One may, however, expect that by increasing the hydration time, the
amount of aluminum released to water will be limited. Although the opinions regarding
the effect of aluminum on living organisms are inconsistent [16], the subsequent re-
search should regard the possibilities of this metal release to water. Moreover, the au-
thors plan to evaluate the possibilities of using metallic calcium instead of aluminum in
further research.

The increasing specific electrolytic conductivity observed in the case of distilled
water and filters from F2 to F6 results (except for the increase in hardness) probably
from higher concentrations of divalent iron (and to a very small extent from trivalent
iron, the concentration of which should be slight in the conditions of such high pH and

low redox potential) and divalent manganese released from the filters characterized by higher contents of metallic iron which was used in the form of a powder. It is also caused by the increasing amount of chlorides in the water, which as indicated iny Table 2 may both be the component of calcium carbonate and metallic iron.

T a b l e 6

Physicochemical parameters and the concentrations of chemical substances
in the treated water flowing through the filters

Parameter	Contaminated water	Water after flowing through the filter					
		Filter					
		F1	F2	F3	F4	F5	F6
pH	6.73	12.36	12.32	12.41	12.40	12.37	12.42
Conductivity, mS/cm	0.843	7.87	7.93	8.09	8.43	8.32	8.03
Redox potential, mV	180	−135	−131	−128	−117	−127	−116
Temperature, °C	19.8	19.8	19.9	19.5	20.0	19.8	20.3
Temporary hardness, mg $CaCO_3/dm^3$	<5	735.52	701.07	718.74	736.95	699.11	736.59
Total hardness, mg $CaCO_3/dm^3$	18.03	800.31	758.01	805.30	774.78	749.44	790.31
Calcium hardness, mg/dm^3 Ca as $CaCO_3$	<5	716.06	749.80	734.09	729.63	718.21	739.62
Fe^{2+}, mg/dm^3	<0.02	0.07	0.16	0.21	0.19	0.22	0.23
Fe_{tot}, mg/dm^3	0.03	0.11	0.17	0.31	0.28	0.27	0.28
Fe^{3+}, mg/dm^3	–	0.04	0.01	0.10	0.09	0.05	0.05
Cu_{tot}, mg/dm^3	1.18	0.11	0.07	<0.04	0.05	<0.04	<0.04
Cr^{6+}, mg/dm^3	0.167	<0.01	0.059	<0.01	<0.01	0.021	<0.01
Ni_{tot}, mg/dm^3	0.443	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Co_{tot}, mg/dm^3	0.524	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Zn_{tot}, mg/dm^3	1.42	0.48	0.68	0.30	0.74	0.67	0.41
Mn_{tot}, mg/dm^3	0.015	0.023	0.054	0.187	0.226	0.218	0.200
SO_4^{2-}, mg/dm^3	64	<2	<2	<2	4	<2	<2
Cl^-, mg/dm^3	227.20	142.45	157.73	204.81	191.80	218.48	173.70

The analysis of distilled water flowing through the filters (Table 5) exhibits that the filters do not release copper, chromium(VI), nickel, cobalt, zinc and sulfates to the water environment. The concentrations of all the substances analyzed in the trials (except for the concentration of copper and zinc in F4, nickel and cobalt in F5, which could have been a result of: sample contamination, presence of substances interfering with the spectrophotometric measurement and the release of these metals from metallic iron which may contain these elements (see Table 2) were lower than the limit of detection of the used measurement methods.

Similar dependencies and changes in the physicochemical parameters and iron and manganese concentrations, observed in the case of distilled water flowing through the

filters, have also occurred in the case of contaminated water (Table 6). The only differ-ence was the efficient removal of sulfates and heavy metals.

The concentrations of Cu, Cr^{6+}, Ni, Co, Zn that pose a hazard to the water environ-ment in high concentrations have been reduced after passing through the filter – some of them even to the level below the detection limit of the spectrophotometer. Zinc was the most difficult to remove, which is probably related to the occurrence of $[Zn(OH)_4]^{2-}$ ions above pH 11. Similarly, above pH 7.5, $[Cr(OH)_4]^-$ ions form with Cr(III). No in-crease in the concentration of chromium was noted because only the contents of Cr(VI), especially hazardous to living organisms, was analyzed which was nearly completely removed from the water. A high flow rate of water through the filters and resulting too short contact time between might also be the reason for the incomplete removal of metal ions.

Only the concentrations of copper ions decreased with the increase in the content of metallic iron powder in the filters' composition. The differences and the concentrations at the output of the filters were so low that it was impossible to confirm that they resulted from the impact of metallic iron. As for the remaining metals, it has been noted that the additives of metallic iron and calcium carbonate did not influence the concentrations of metallic ions

In this context, it is evident that the materials responsible for the formation of strongly basic and reductive conditions were CaO and Portland cement. These constit-uents were essential in the removal of metal ions and reduction of sulfates to sulfides. The use of these materials resulted in the release of hydroxides and Ca and Mg bicar-bonates and the probable precipitation of metals and sulfides in the porous space of the filters.

In the evaluation of the impact of metallic iron and calcium carbonate additives which change the reactivity of the filters on other technical parameters (Table 4), it has been noted that they cause an increase in the bulk density (especially in the case of filter F6 characterized by the content of 5 wt. % of metallic iron), while a larger amount of metallic iron changes the effective porosity and the hydraulic conductivity to a much lesser degree than it is in the case of calcium carbonate. To a degree lesser than in the case of cement, both additives also impact the single-axis compressive strength of filter samples. That impact is larger in the case of higher metallic iron contents than it is in the case of calcium carbonate.

In the analysis of strength losses in samples subject to freezing as well as freezing and action of 3% NaCl solution (Table 4), no tendencies of changes related to the changes in compositions of the materials comprising the filters were noted.

The specific density of all filters characterized by a given composition (after crush-ing and size reduction) changes in line with the participation of individual components comprising the filter (Table 4). That means that the specific density increases upon in-creasing the amount of metallic iron on one hand and Portland cement and aluminum powder on the other.

4. CONCLUSIONS

• To achieve mechanical strength allowing safe transport, storage and installation of the filters in their target locations, the minimal contents of the Portland cement should be 15 wt. %. Larger participation of cement allows to achieve higher mechanical strength and does not affect the basic function of the filter – it does, however, increase the production costs.

• The content of aluminum powder should be 0.2 wt. %, which allows achieving hydraulic conductivity at the level of 5.11×10^{-4} m/s. Aluminum powder contents below that value resulted in the decrease of the hydraulic conductivity and successive loss of water permeability.

• The filters analyzed in the work exhibit high efficiency in the removal of metals (copper, chromium(VI), nickel, cobalt, zinc) from the precipitation water.

• Metallic iron and calcium carbonate additives, which were supposed to increase the reactivity of the filters and increase the efficiency in the removal of metal ions from water, only caused a decrease in the concentration of copper ions. The use of these materials turned out to be unreasonable.

• A durable and water-permeable filter exhibiting a high level of metal and sulfate reduction in precipitation water should contain 10 wt. % of calcium oxide, 28 wt. % of water, and 1.8 wt. % of anhydrous calcium sulfate. Te contents of remaining materials should amount to 45 wt. % of quartz sand to increase the mechanical strength, resistance to frost and stability of the filters, 15 wt. % of the Portland cement to achieve the required strength and 0.2 wt. % of aluminum powder for proper water permeability,

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