CHEMIJA. 2015. Vol. 26. No. 2. P. 84–92

Chromium containing sludge from metal surface treatment processes: stabilization in a ceramic body

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The effectiveness of stabilization of chromium containing sludge from metal surface treatment processes in a low-melting hydromicaceous clay ceramic body has been estimated. Only the chromium contained in the chromium electroplating process sludge may be stabilized in the hydromicaceous clay ceramic body with 5% and 10% of such sludge additive fired at 1 050 °C to 94.18 and 70.06%, respectively. Stabilization of sludge from the chromate conversion coating process at low temperatures which are typical of easily fusible hydromicaceous clay products is not effective, although the amount of chromium in leachate from the ceramic body with addition of this sludge decreases as the temperature is increased. Therefore the chromium contained in chromate conversion coating sludge is stabilized with the effectiveness of 32.47–79.30% in the ceramic body with addition of 10% of kaolin fired at 1 075–1 100 °C.

Key words: electroplating sludge, chromium leachate, ceramic body, firing temperature

INTRODUCTION

In order to improve mechanical properties and corrosion resistance qualities of metal surfaces, they are correspondingly treated. Most often these properties are improved by chromium electroplating and chromate conversion coating processes using chromic acid and its salts. The first of them is an electrochemical process during which a surface is covered with chromium using an electrolytic process [1]. The other is a conversion process during which a metal surface is coated with an insoluble chromate layer. As a result of reactions going on during this process, the active metal surface is coated with an inert film [2]. From the point of view of technology it is a perfect solution to improve the quality of metal, although wastewater generated during such processing of metal surface contains hazardous compounds of chromium Cr^{6+} [3, 4].

Wastewater from metal surface treatment is usually treated using physical and chemical methods. At first the wastewater is acidized. This is followed by a chemical chromium reduction with sulfite compounds, ferrous metals waste or ferrous sulfate with $pH \leq 2.5$ [5]. During this process Cr^{6+} is reduced to Cr^{3+}. At the next stage the wastewater is neutralized by sodium hydroxide or hydrated lime so that Cr^{3+} (and other metals) would precipitate in the form of insoluble hydroxide $Cr(OH)_3$.

Chrome (and other heavy metals) in the generated sludge is very mobile which may determine conversion of the metal into a more hazardous form [6]. For this reason it is classified to the hazardous waste class and therefore may not be disposed of at the landfills [7]. In the EU countries there are 4 000 metal surface finishing industrial businesses which produce about 150 000 t of sludge per year [8]. The amount of chromium in this sludge varies approximately from 1 to 23% [9]. It is known that hydroxides of heavy metals contained in the sludge decompose at high temperature with formation of significantly more stable compounds in the structure of which these metals are incorporated. Therefore researches are made to stabilize waste containing hazardous metal compounds in thermally treated ceramic matrices [10, 11]. Obtained products would be used as ceramic construction materials and this would also allow reducing expenses on production of ceramic products [12]. Ferreira et al. [10] state that sludge additives for red plastic clay (which main components are illite and smectite) ensure effective stabilization of heavy metals. Karlovic et al. [11] confirm that ions of heavy metals (copper, nickel, iron, lead, manganese and zinc) are stabilized during thermal treatment using domestic (not hydromicaceuos) clay, but at the same time reject effective

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stabilization of compounds. The main objective of this study is to estimate chromium stabilization efficiency in the ceramic body of easily fusible hydromicaceous clay.

EXPERIMENTAL

Sludges from three different Lithuanian metal surface treatment companies were used for this work. Two of them, *B* (JSC Baltic Industrial Coating, Vilnius) and *I* (JSC Inlook Vilnius, Vilnius), are from the chromate conversion coating process and the third sludge, *K* (JSC Bangos Energetika, Kaunas), is from the galvanic electroplating process. The composition of sludge is shown in Table 1. The sludge was dried at the temperature of 105–110 °C and further ground in a mill to particles smaller than 0.063 mm.

Table 1. **Element content of untreated electroplating sludge, %**

Element	Sludge		
	B	*I*	*K*
C	14.07	10.77	6.00
O	41.63	42.87	30.54
Al	1.25	8.74	2.86
Na	0.50	0.84	3.71
Mg	0.25	1.03	3.77
P	7.70	6.90	3.31
S	0.73	0.80	0.17
Ca	19.81	6.71	10.53
Cr	2.70	2.62	1.25
Fe	0.37	0.72	10.92
F	9.32	17.78	0.25
Si	0.31	0.25	1.51
Cu	0.37	0.32	0.76
Cl	0.28	–	1.83
Zn	0.38	–	21.3
Ni	–	–	1.29

To determine change of the mineral composition during firing and leaching chromium all the sludge samples were fired in a lab furnace SNOL 30/1300 with a programmed controller E5CK-T ensuring temperature bias not exceeding ±1 °C. The temperature was being increased up to 120 °C at 200 °C/h rate, then the material was hold at this temperature for 20 minutes and then up to the chosen temperature at 500 °C/h rate.

Clay from the Girininkai pit (Lithuania) was dried at 105–110 °C, then ground in a dismembrator to smaller than 1 mm sized grains. Kaolin (Czech Republic) was used as an additive to increase the sample firing temperature. The average chemical compositions of the clay and kaolin are provided in Table 2.

Illite and muscovite minerals prevail in the clay, and there is also kaolinite and a big amount of SiO_2 in the form of quartz sand as well (Fig. 1, pattern 1). Calcite, dolomite and feldspar are found among nonplastic admixtures. The main crystalline phase of kaolin is kaolinite, quartz, halloysite and hydromica group mineral – illite (Fig. 1, pattern 2).

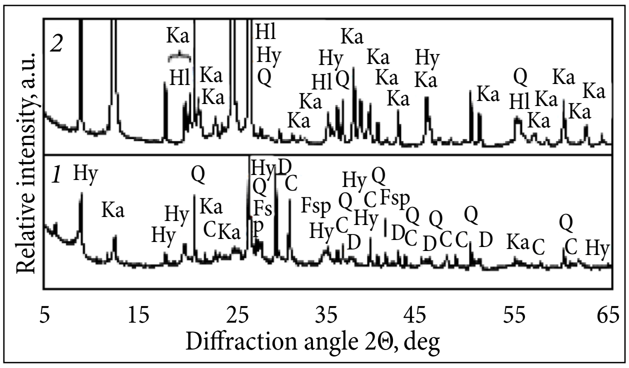

Fig. 1. X-ray diffraction patterns of clay (*1*) and kaolin (*2*). Indexes: Q – quartz, Hy – hydromica, Ka – kaolinite, Fsp – feldspar, D – dolomite, C – calcite, Hl – halloysite

In order to determine the influence of the amount of sludge additive on chromium leaching from the sludge stabilized in a ceramic body 5 and 10% of sludge was mixed into the clay mass. Therefore, in order to increase the firing temperature of samples 10% (BK1) and 45% (BK2) of kaolin was added to the molding clay mix with 10% of sludge B.

Preparing samples the amounts of dry powder of clay and additives were mixed for one hour. Then water was poured into the mixtures for preparation of a plastic forming mass with humidity of 19–25%. Slabs of the size 60 × 30 × 10 mm were formed from this mass, dried at 105–110 °C and fired in a laboratory furnace. The firing temperature of the samples with sludge additive was 900, 1 000, 1 025 and 1 050 °C, while the duration of isothermal exposure at the desirable temperature was 1 and 4 h. The samples with sludge and kaolin additives were fired at 1 050 °C temperature for 1 and 4 h and at 1 075, 1 100, 1 125 °C temperatures for 1 h. The firing temperature interval for experiments was chosen considering the usual temperature used in Lithuanian industry for firing ceramics from easily fusible clays.

The X-ray powder diffraction (XRD) data were determined with a DRON-6 powder X-ray diffractometer with Bragg–Brentan geometry using Ni-filtered Cu Kα radiation and graphite monochromator. The step-scan covered the angular range 5–60° (2θ) in steps of 2θ = 0.02°.

IR spectra were carried out with the help of a spectrometer PerkinElmer FT-IR system Spectrum X. Specimens were prepared by mixing 1 mg of the sample in 200 mg of KBr.

Table 2. **Chemical composition of clay and kaolin, % of mass**

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MnO	MgO	Na_2O	K_2O	LOI
Clay	47.69	0.76	13.35	6.19	9.05	0.06	3.59	0.96	3.32	11.9
Kaolin	54.82	–	33.91	0.74	0.06	–	0.42	0.34	1.27	8.44

The spectral analysis was performed in the range of 4 000–400 cm^{-1} with spectral resolution of 1 cm^{-1}.

Before selection of an eluent for chromium leaching tests, the influence of the eluent pH to the leaching of this element was investigated at first. It was found that in the range of pH 4–9 it has a minimal impact on the leaching efficiency. Since the ceramic body with stabilized chromium would be used in the manufacturing of building ceramics, the main leaching from manufactured products is carried out under the influence of rainfall. pH of rain water is about 6. Distilled water in the open air absorbs carbon dioxide and so pH is reduced immediately (which acidifies). Therefore it was decided to choose distilled water as an eluent. Chromium concentration in the leachate was determined with an atomic absorption spectrometer SHIMADZU AA-6800. The absorption was measured at the wavelength of 357.9 nm. Before measuring 5 g of sludge was mixed with 50 ml of distilled water, while the samples were poured with 100 ml and soaked for 24 h shaking with a lab shaker. The mixture was then filtered through the fiberglass filter paper.

Chemical composition of raw materials was determined by a Bruker X-ray energy dispersion spectrometer (EDS) XFLASH 4030 of a scanning electron microscope FEI Quanta 200 FEG.

RESULTS AND DISCUSSION

X-ray diffraction analysis

Unfired sludge has an amorphous structure and it contains only a small amount of the crystal phase (Fig. 2a–c, pattern 1). The diffraction pattern of sludge *B* identified peaks typical of fluorapatite $Ca_5(PO_4)_3F$ and calcite $CaCO_3$, of sludge *I* for gypsum $CaSO_4 \cdot 2H_2O$, and of sludge *K* for calcite. The $CaCO_3$ peaks in the diffraction pattern of sludge *K* are more intensive than in the pattern of sludge B (Fig. 2a, c, pattern 1). Due to a small amount of chromium (1.25–2.70%) (Table 1) no compounds with this element were identified by the X-ray diffraction analysis in any of the sludge samples. The sludge *K* diffraction pattern does not show any compounds the structure of which would include Zn, although its amount in this sludge sample is quite considerable (21.3%). Since in the case of precipitation of the wastewater with hydrated lime most metals precipitate in the form of hydroxide it is likely that Zn has incorporated into the amorphous $Zn(OH)_2$ structure.

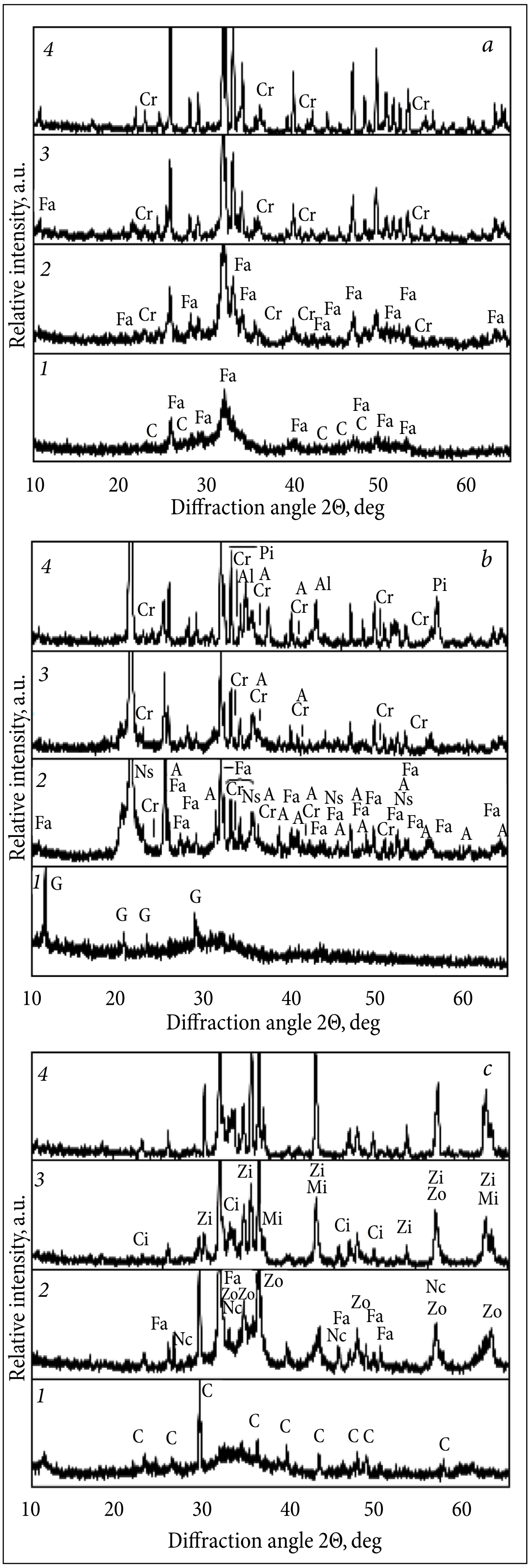

Fig. 2. X-ray diffraction patterns of sludge *B* (*a*), *I* (*b*) and *K* (*c*): unfired (*1*) and fired at 600 °C (*2*), 800 °C (*3*) and 1 050 °C (*4*) for 1 h. Indexes: C – calcite, Fa – fluorapatite, Cr – chromium (3$^+$) oxide, G – gypsum, A – anhydride, Ns – sodium aluminosilicate, Al – aluminium oxide, Pi – potassium ferrous oxide, Zo – zinc oxide, Nc – sodium chloride, Ci – calcium ferrite, Mi – magnesium ferrite, Zi – zinc ferrite

Peaks typical of fluorapatite are expressed on the diffraction patterns of all the sludge samples fired at the temperature of 600 °C (Fig. 2a–c, pattern 2) and they become more intensive as the temperature increases. Most of this compound is found in sludge *B*, while the least amount is found in sludge *K* (Fig. 2a–c, patterns 2–4). After the dehidratation of gypsum at 250 °C the anhydrite $CaSO_4$ was formed [13] (Fig. 2b, patterns 2–4). Carbonates contained in sludge *B* completely decompose at 800 °C, while in sludge *K* insignificant calcite peaks can still be seen at this temperature. After the decomposition of carbonates in sludge *K* fired at the temperature of 800 °C and higher several spinel structure compounds are formed, $CaFe_2O_4$, $ZnFe_2O_4$ and $MgFe_2O_4$ (Fig. 2c, patterns 3–4). On the diffraction patterns of sludge *K* fired for 1 h at the temperatures of 600–1 050 °C ZnO peaks dominate (Fig. 2c, patterns 2–4).

According to the results of X-ray diffraction analysis chromium oxide Cr_2O_3 was formed during firing in sludge *B* and sludge *I* samples. As the temperature of firing of these sludge samples rises from 600 to 1 050 °C the intensity of Cr_2O_3 peaks increases and this means that its amount in the sludge grows (Fig. 2a, b, patterns 2–4). It should be noted that the diffraction patterns of sludge *I* show only traces of this oxide (Fig. 2b, patterns 2–4).

Leaching of chromium

It has been determined that firing temperature has significant influence on leaching of chromium from sludge. The AAS analysis shows that 6.96 mg/kg and 9.44 mg/kg of chromium are leached from unfired chromate conversion coating sludge samples *B* and *I*, respectively (Table 3). Yet, 7–8 times more chromium is leached from sludge *K* received during the process of chromium electroplating of metals (72.01 mg/kg). It can be stated that in the latter sludge not all Cr^{6+} was reduced into Cr^{3+} and precipitated in the form of $Cr(OH)_3$ during wastewater reduction and neutralization.

Even greater amounts of leached chromium are found in all the sludge samples fired for 1 h at the temperature interval of 400–800 °C (Table 3). The maximal amount of leached chromium from sludge samples *B* and *I* was determined after they were fired at 600 °C, and from sludge sample *K* at 700 °C (Table 3). Leaching of chromium from sludge *B*, as compared with that determined at the temperature of 400 °C, was increased by 1.43 times, from sludge *I* by 2.36 times, and from sludge *K* by 1.27 times. It is known that in the presence of alkali Cr^{3+} is unstable and may be easily oxidized to Cr^{6+} [14]. Oxidation starts at the temperature of 200–300 °C and approaches its maximum at the temperature interval of 600–800 °C. At higher temperatures Cr^{6+} reduction back into Cr^{3+} starts and for this reason the amount of leaching of chromium from synthetic mixtures decreases [15]. These statements and results of leaching from sludge *B* and sludge *I* samples (especially from *B*) are confirmed by the presence of Cr_2O_3 (insoluble) determined in these sludge samples by X-ray diffraction analysis. At the temperature of 600 °C its amount is the lowest, this means that chromium has incorporated into the structure of other, soluble, compounds (the amount of chromium in leachate is the greatest). As the temperature of sludge firing increases, more and more chromium incorporates into Cr_2O_3, therefore the amount of leached chromium decreases (Fig. 2a, b, patterns 2–4, Table 3). Leaching of chromium from sludge *K* starts to decrease only after its firing at 800 °C, and still not to such a considerable degree as in other sludge samples. Nevertheless, even after the firing at 1 050 °C almost 13 times more chromium is leached from sludge *K* than from natural sludge.

IR spectral analysis

By comparing to IR spectra of unfired sludge, it has been noticed that in all unfired sludge samples in the 2 800–3 600 cm^{-1} frequency range OH stretching vibrations a wide absorption band in the 3 420 cm^{-1} area is noticeable which describes vibrations of OH groups interconnected by hydrogen bonds (Fig. 3a–c, curve 1). The latter as well as 1 643 cm^{-1} bands are typical of crystallized water and show that non-fired sludge contains a considerable amount of metal hydroxides [16, 17]. After sludge has been fired at 600 °C, the intensity of these bands decreases strongly which signs decomposition of metal hydroxides. Vibrations in 1 484–1 419 cm^{-1} and 879 cm^{-1} frequency ranges are attributable to CO_3^{2-} group stretching vibrations, while in 712 cm^{-1} frequencies range to deformation vibrations [17, 18]. It has been noticed that absorption bands in these frequency areas are more intensive (as expected) in the sludge *K* spectrum (Fig. 3a–c). Absorption bands typical of carbonates are rather intensive in sludge *B* as well. It is interesting that rather clear absorption bands typical of carbonates remain in the spectrum of sludge *K* fired at 800 °C and even at 1 050 °C, which means that they have not yet fully decomposed at these temperatures (Fig. 3c, curves 3 and 4). According to Nafisah et al. [19] the remaining carbonates may fully decompose at the temperature above 1 100 °C. In the sludge *B* and sludge *I* samples fired at 800 °C there

Table 3. **Amount of chromium leached from unfired and fired at various temperatures sludge, mg/kg**

Sludge	Concentration of chrome, mg/kg								
	Firing temperature, °C (duration of firing 1 h)								
	20	400	600	700	800	900	1 000	1 025	1 050
B	6.96	2 255.78	3 247.59	2 455.43	698.75	359.77	106.91	51.03	9.93
I	9.44	1 082.16	2 561.25	1 117.21	586.93	255.15	129.38	21.15	11.99
K	72.02	2 117.99	2 707.79	3 300.34	2 778.77	2 411.20	1 117.57	1 041.02	959.38

are no bands typical of carbonates because carbonates have already decomposed (Fig. 3a, b, curve 3).

Absorption bands typical of $[PO_4]^{3-}$ vibrations are seen in the IR spectra of all the three sludge samples (Fig. 3a–c). A wide absorption band in the range of 1 100–1 000 cm^{-1} and 965 cm^{-1} frequencies is assigned to tetrahedral structure stretching vibrations, two smaller bands in 605 and 562 cm^{-1} and insignificant ones in 471 cm^{-1} frequency range are typical for deformation vibrations in the apatite structure [17, 20].

The absorption band in 1 115–1 132 cm^{-1} frequency range in the sludge *I* spectra confirm that it contains sulphate group compounds, since this band is typical of SO_4^{2-} group stretching, and in 677 cm^{-1} frequency range it is typical of deformation vibrations (Fig. 3b, curves 2–4) [21, 22]. Absorption bands 449–492 cm^{-1} may be assigned to symmetrical stretching SO_4^{2-} vibrations [23].

In the spectra of sludge *K* fired at the temperature interval of 600–1 050 °C the absorption band in the 450–500 cm^{-1} frequency range with the greatest intensity around 450 cm^{-1} is typical of Zn–O bonds [24] and confirms the results of XRD analysis that at such temperatures Zn oxide is formed in the sludge (Fig. 3c, curves 2–4). The absorption band at 520 cm^{-1} typical of Fe–O stretching vibrations may be attributed to $ZnFe_2O_4$ in the sludge structure [25, 26].

Absorption bands in 605 and 562 cm^{-1} frequency range are typical both of $[PO_4]^{3-}$ vibrations and of the Cr–O bond. Yet, in the sludge *B* and *I* IR spectra it is seen that from 600 °C the absorption band near 562 cm^{-1} splits into two. There appear additional vibrations in the 572 cm^{-1} frequency range which is typical exactly of the Cr–O bond (Fig. 3a, b, curves 2–4). Also in the spectrum of sludge *B* there is a low intensity band in the 428 cm^{-1} frequency range, which confirms that during firing Cr_2O_3 is formed in this sludge. No such band is seen in sludge *I*, because it is covered with more intensive SO_4^{2-} group vibrations, although an expressed band in 634 cm^{-1} frequency range says that there is Cr_2O_3 in sludge [27, 28].

Chromium stabilization in ceramic body

X-ray diffraction analysis

The X-ray diffraction analysis of the ceramic body with addition of 5 and 10% of various sludge additive fired at the temperature interval of 900–1 050 °C showed that as the amount of additive and firing temperature increased, the mineral composition of the ceramic body did not change, only the intensity of peaks typical of the formed compounds changed (Fig. 4). All the patterns clearly show peaks typical of quartz which intensity decreases as the firing temperature rises because quartz at high firing temperatures actively participates in the sintering process of the ceramic body, including formation of thermally stable compounds, anorthite $CaAl_2Si_2O_8$ and hedenbergite $CaFeSi_2O_6$. In the ceramic body with additive of sludge *B* and sludge *I* hematite Fe_2O_3 was formed and its amount increases as the ceramic body firing temperature rises (Fig. 4a, b). Peaks typical of hematite

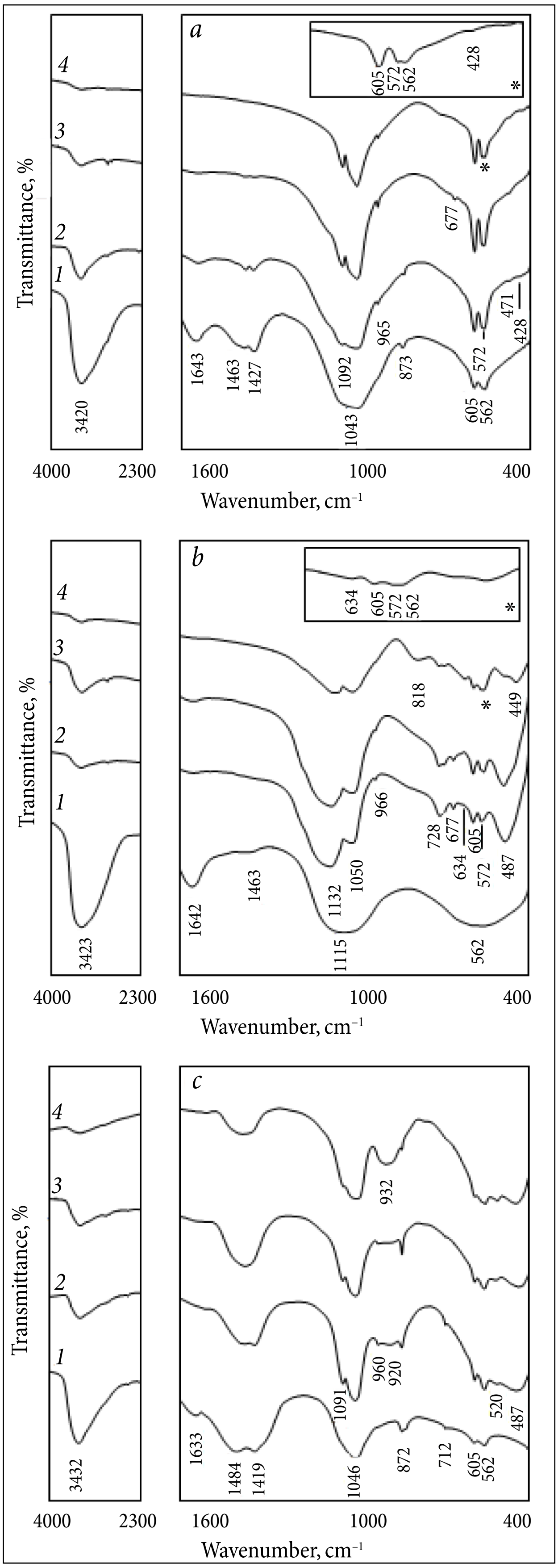

Fig. 3. FT-IR spectra of sludge *B* (*a*), *I* (*b*) and *K* (*c*): unfired (*1*) and fired at 600 °C (*2*), 800 °C (*3*) and 1 050 °C (4) for 1 h

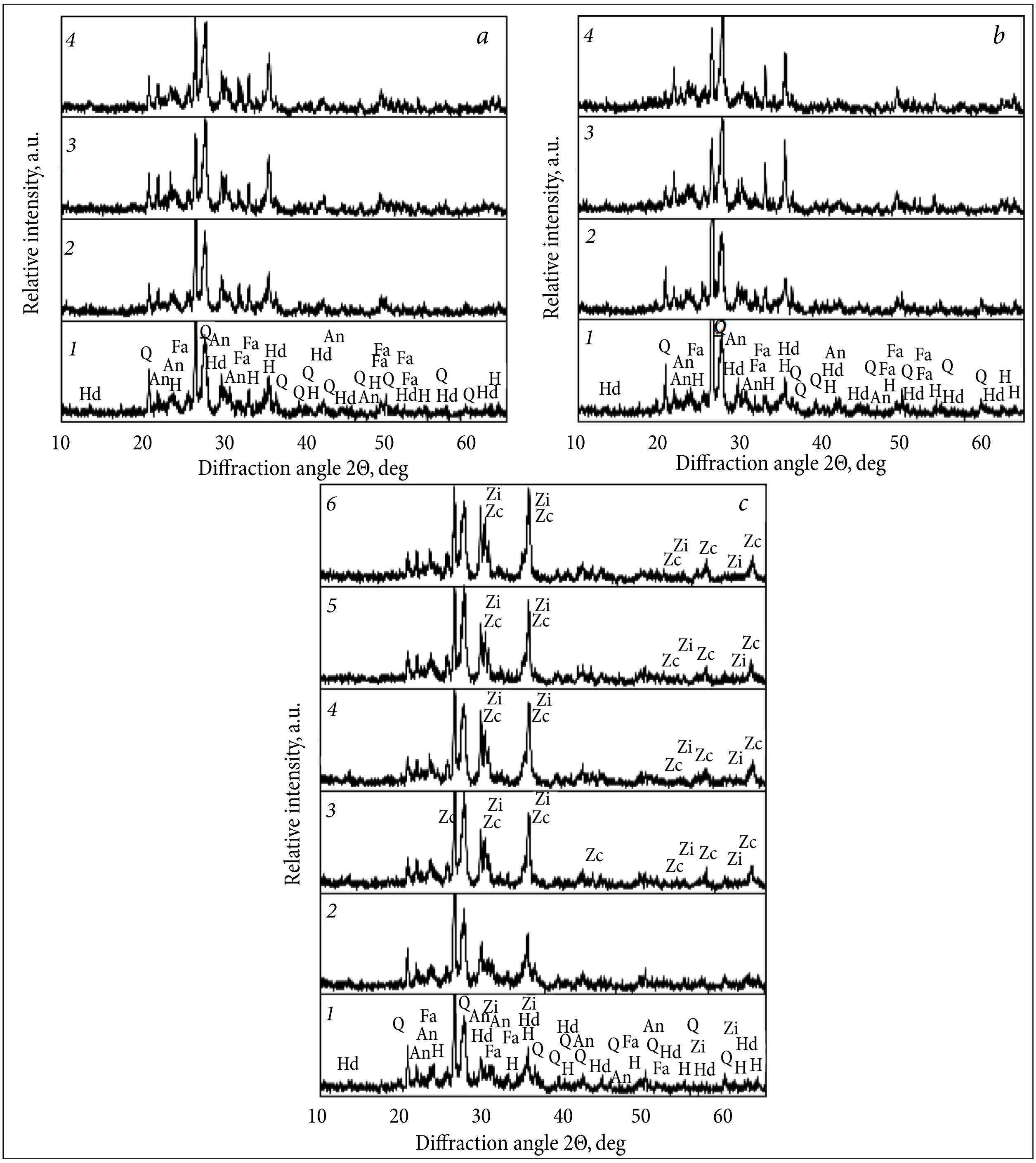

Fig. 4. X-ray diffraction patterns of the ceramic body with additive of sludge B (*a*), I (*b*) and K (*c*) fired at 900 °C (*1*, *2*), 1 000 °C (*3*, *4*) and 1 050 °C (*5*, *6*) for 1 h. Amount of additive: 5% (*1*, *3*, *5*) and 10% (*2*, *4*, *6*). Indexes: Q – quartz, Hd – hedenbergite, An – anorthite, H – hematite, Fa – fluorapatite, Zi – zinc ferrite, Zc – zinc chromite

are more intensive on the diffraction patterns of the ceramic body with additive of sludge *I*, although the amount of iron in sludge *B* and sludge *I* is very similar (Table 1). In the ceramic body with sludge *B* less iron incorporates into this oxide and more iron in the structure of hedenbergite $CaFeSi_2O_6$ (Fig. 4a, b). In the ceramic body with additive of sludge *K* iron incorporates into the $ZnFe_2O_4$ structure, so even less hematite is formed in this body than in the one with sludge *B* (Fig. 4a, c). The bigger amount of sludge *K* in the body and the higher the firing temperature, the more $ZnFe_2O_4$ and the less hematite Fe_2O_3 is formed (Fig. 4c, pattern 1–6). In the ceramic body fired at 1 000 °C with 5 and 10% of sludge *K* additive another spinel structure oxide is formed – that is zinc chromite $ZnCr_2O_4$, the amount of which, like of $ZnFe_2O_4$, increases as the amount of sludge and the firing temperature rise (Fig. 4c, patterns 3–6).

IR spectroscopy

Changes of the mineral composition of ceramic bodies with addition of different sludges that occurred as the samples fired at the temperatures of 900–1 050 °C are also obvious in their IR spectra. The spectra confirm the results received during the X-ray diffraction analysis. In all IR spectra of the ceramic body with 5 and 10% of additive absorption bands of Si–O bond stretching vibrations are identified in the 800–1 200 cm^{-1} frequency range: 1 050 cm^{-1}, 794 cm^{-1}, 774 cm^{-1} (doublet) and in the deformation vibrations range: 692 cm^{-1} typical of $[SiO_4]^-$ tetrahedral internal vibrations which confirms that there is quartz in the ceramic body [29, 30] (Fig.5). The absorption bands 730 and 578 as well as 539 cm^{-1} typical of $[SiO_4]^-$ tetrahedral internal vibrations and the 920 cm^{-1} shoulder in the symmetrical and asymmetrical stretching Si–O vibrations range sign formation of anorthite [31, 32]. Formation of hedenbergite in the ceramic body is confirmed by the 663 cm^{-1} absorption band, since bands describing symmetrical and asymmetrical stretching Si–O bond vibrations in the 800–1 200 cm^{-1} frequency range are typical of most silicate compounds [33] and it is difficult to identify hedenbergite in this part of the IR spectrum (Fig. 5). Absorption bands in 539 cm^{-1}, 520 cm^{-1} and 465 cm^{-1} frequency range are typical of Fe–O vibrations [26, 29] and show that hematite and ferrous oxide are formed in ceramic bodies (Fig. 5). Just like the absorption band in the unfired sludge, the one in the 605 cm^{-1} frequency range is typical of asymmetrical PO_4^{3-} deformations [17] and confirm that there is fluorapatite in the ceramic bodies. Unfortunately, absorption bands typical of stable chromium compounds were not determined in IR spectra.

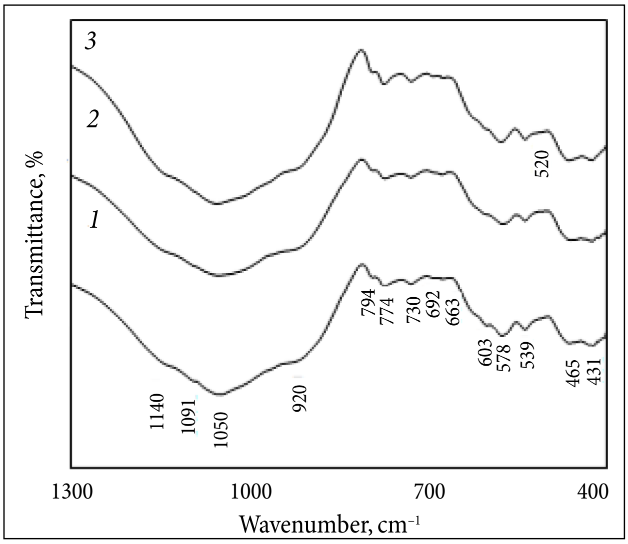

Fig. 5. FT-IR spectra of the ceramic body with 5% of sludge B (*1*), I (*2*) and K (*3*) additive fired at 1 050 °C for 1 h

Leaching of chromium

The amount of chromium leached from the ceramic body depends on the type of added sludge, its amount in the forming mass, firing temperature and duration. The smaller the amount of additive and the higher the firing temperature of a sample, the less chromium is leached from the ceramic body (Table 4). It has been determined that the biggest amount of chromium is leached from the ceramic body with additive of sludge *B*, the least amount is leached from the ceramic body with additive of sludge *K* (Table 4). The amount of chromium leached from sludge decreases significantly after firing the samples at 1 000 °C. For example, leaching of chromium from the ceramic body with 5% of sludge *B* fired at this temperature for 1 h decreases by 79.74%, with the same amount of sludge *I* it decreases by 70.63%, and with sludge K by 81.71%. The amount of chromium leached from ceramic bodies fired at 1 025 and 1 050 °C with addition of sludge consistently decreases.

It has been determined also that the higher the firing temperature, the more the difference between the amounts of chromium leached from a ceramic body with addition of 5 and 10% of sludge (Table 4). For example, after 1 h of exposition at 900 °C 1.03 times more chromium was leached from the ceramic body with 10% of sludge *B* than from the body with 5% of this additive, after firing at 1 000 °C 1.46 times more, at the temperature of 1 025 °C 2.11 times more and after firing at 1 050 °C 4.18 times more chromium was leached. The same dependence of the amount of leached chromium from the firing temperature was determined in ceramic bodies with 5 and 10% of sludge *I* and *K* additive.

Leaching of chromium from the ceramic body with the sludge additive also depends on the duration of firing: the longer the sample is fired, the less chromium is determined in its leachate (Table 4). The least difference between the amount of chromium leached from the body fired for 1 and 4 h is for that with sludge *K*. This difference, depending on

Table 4. **Leaching of chromium from a ceramic body with sludge additive fired at various temperatures, mg/kg**

Slabs with	Concentration of chrome, mg/kg						
	Firing temperature, °C – duration of firing, h						
	900–1	900–4	1 000–1	1 000–4	1 025–1	1 025–4	1 050–1
5% of sludge B	350.87	336.97	71.09	68.25	32.53	31.18	6.61
10% of sludge B	361.63	353.30	103.71	99.47	68.63	67.73	27.61
5% of sludge I	166.96	127.03	49.04	39.74	12.50	11.32	10.45
10% of sludge I	230.76	218.49	76.40	54.01	33.52	29.98	28.75
5% of sludge K	58.40	55.68	10.68	9.75	6.48	5.87	4.19
10% of sludge K	156.36	150.32	47.17	45.68	32.38	31.91	21.56

the amount of the additive and on the temperature of firing, changed from 1.45 to 9.41%. It has been noticed that the higher the temperature of firing the ceramic body with addition of sludge *B* and sludge *I* is, the greater the difference between the amounts of chromium leached from the ceramic body fired for 1 and 4 h is. 3.96% less chromium is leached from the ceramic body with 5% of the sludge *B* additive fired for 4 h at 900 °C than from the one fired for 1 h, whereas after firing for 4 h at 1 025 °C 30.34% less chromium is leached than in the case of firing for 1 h.

Comparing to the amount of chromium leached from the ceramic body with sludge additives and its amount leached from the unfired sludge it has been noticed that only chromium contained in sludge *K* was stabilized in the ceramic body fired at various temperatures (except for the samples with 10% fired at 900 °C) (Tables 3 and 4). The amount of chromium leached from the samples with 5% of sludge additive fired at this temperature is 23.30–22.68% smaller than that from the unfired sludge (1 and 4 h), and after firing at 1 050 °C it is even 94.18% smaller. Chromium in 10% of sludge *K* was stabilized in the ceramic body fired at 1 000 °C and higher. After firing a sample with 10% of *K* additive at this temperature 34.50–36.54% of chromium is leached, while after firing at 1 050 °C 70.06% less than from unfired sludge. Chromium is stabilized in zinc chromite which is formed in the ceramic body during firing. As the firing temperature and the amount of sludge additive increase, more zinc chromite is formed, this explains why leaching from the sludge decreases (Fig. 4c, patterns 3–6). However, results showed that stabilization of chromium contained in chromate conversion coating sludge (*B* and *I*) in the hydromicaceous clay ceramic body fired at the temperatures of 900–1 050 °C was not effective. Nevertheless, it has also been determined that the amount of chromium leached from the ceramic body with this sludge decreases as the temperature increases.

Therefore, in order to increase the firing temperature of samples 10% (BK1) and 45% (BK2) of kaolin was added to the molding clay mix with 10% of sludge *B* [34]. Samples of the said composition were fired at the temperatures of 1 050, 1 075, 1 100 and 1 125 °C for 1 and 4 h.

It has been determined that the bigger the amount of kaolin in a molding mix is, the more chromium is leached from ceramic bodies fired at the mentioned temperatures (Table 5). The amount of chromium leached from samples BK1 fired at 1 050 °C was 24.48%, and from samples BK2 it was 49.95% more than from the ceramic body without additive of kaolin fired at the same temperature (Tables 4 and 5). Depending on the duration of firing, from 22.4 to 32.47% of chromium is stabilized at 1 075 °C (as compared with the amount leaching from natural sludge (6.96 mg/kg), and at 1 100 °C from 75.59% to 79.30% is stabilized (1 and 4 h). Even after firing at 1 125 °C 54.66% more chromium is leached from this ceramic body than from the unfired sludge (Tables 3 and 5). And the higher firing temperature is, the bigger the difference is between chromium leached from the samples fired for 1 h and for 4 h. Thus, the amount of chromium leached from ceramic body BK1 fired for 4 h at 1 050 °C is 10.53%, at 1 075 °C it is 12.96%, and at 1 100 °C it is 15.29% less than from ceramic bodies fired at these temperatures for 1 h. This difference in the case of ceramic body BK2 is even bigger: 5.44%, 29.0% and 37.32%, respectively (Table 5).

The X-ray diffraction analysis has determined any stable chromium compounds formation of which would reduce the amount of chromium leached from the ceramic body with kaolin additive. In the ceramic body with 10% of kaolin additive (BK1) fired at 1 100 °C for 1 h, just like in the samples without this additive, quartz, anorthite, hematite, hedenbergite and fluorapatite formed. On the diffraction pattern of the ceramic body with addition of 45% of kaolin (BK2) peaks typical of mullite $Al_2Si_6O_{13}$ and spinel $MgAl_2O_4$ prevail.

CONCLUSIONS

It has been determined that the amount of chromium leached from a ceramic body depends on the type of sludge additive, its amount in the molding mass, firing temperature and duration. The less the amount of additive and the higher the firing temperature of sample is, the less chromium is leached from the ceramic body.

Chromium contained in the galvanic chromium plating process sludge may be stabilized in an easily fusible hydromicaceuos clay ceramic body fired at the temperature interval of 900–1 050 °C. Chromium in ceramic bodies with addition of 5% and 10% of this sludge fired at 1 050 °C is stabilized to 94.18% and 70.06%, respectively. It has been determined that chromium incorporates into the structure of $ZnCr_2O_4$ which is formed during firing of the ceramic body at the temperatures of 1 000–1 050 °C.

It has been investigated that stabilization of sludge from chromate conversion coating formation process at low temperatures typical of firing products made of easily fusible hydromicaceous clay is ineffective. Therefore chromium in this sludge is stabilized with efficiency of 32.47–79.30% in the ceramic body with addition of 10% of kaolin fired at the

Table 5. **Leaching of chromium from samples with kaolin addition, mg/kg**

Sample	**Concentration of chrome, mg/kg**						
	Firing temperature, °C – duration of firing, h						
	1 050–1	**1 050–4**	**1 075–1**	**1 075–4**	**1 100–1**	**1 100–4**	**1 125–1**
BK1	34.37	30.75	5.40	4.70	1.70	1.44	Slab deformation
BK2	55.17	52.17	45.39	32.18	29.39	18.42	15.35

temperatures of 1 075–1 100 °C. If the amount of kaolin is increased to 45%, chromium in the ceramic body is no more stabilized: 54.66% more chromium is leached than from unfired sludge (at 1 125 °C).

Received 30 January 2015
Accepted 13 February 2015

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METALO PAVIRŠIAUS APDOROJIMO PROCESO DUMBLE ESANČIO CHROMO STABILIZAVIMAS KERAMINĖJE ŠUKĖJE

Santrauka

Nustatytas chromo turinčio metalų paviršiaus apdorojimo dumblo stabilizavimo žemos lydymo temperatūros hidrožėrutinio molio keraminėje šukėje efektyvumas. Efektyviai (94,18 ir 70,06 %) stabilizuojamas tik elektrolitinio chromavimo nuotekų valymo dumblas, kai jo kiekis keraminėje šukėje sudaro 5 ir 10 %, o šukės degimo temperatūra ne žemesnė už 1 050 °C. Aliuminio konversinio dengimo chromu dumblo stabilizavimas panašiomis sąlygomis nėra efektyvus, nors didinant degimo temperatūrą iš keraminės šukės išplaunamo chromo kiekis mažėja. Pastarąjį chromo turintį dumblą galima efektyviau stabilizuoti (32,47–79,30 %) į hidrožėrutinio molio formavimo mišinį papildomai pridedant 10 % kaolino, o pačią šukę degant 1 075–1 100 °C temperatūrų intervale.

Autoriai labai dėkingi UAB „Baltic Industrial Coating“, UAB „Inlook – Vilnius“ ir UAB „Bangos energetika“ už pateiktus tyrimams reikalingus atliekų ėminius.