Stability of Ceramic Glazes Obtained by Valorification of Anorganic Pigments Extracted from Electroplating Sludge

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This paper presents the results of the research activity in order to etablish the stability and leaching potential of ceramic tiles which have been developed using glazes colored with pigments obtained by the extraction of chromium and iron metals from electroplating sludge. All these ceramic tiles contain various amounts of heavy metals in their glazes due to the pigments composition. The ceramic samples have been subjected to leaching tests in order to detect if various elements of relevance such as chromium, lead, cadmium, zinc or iron migrated to any great extent into test solutions. Leaching tests have been performed following the international standard SR ISO 10545-15 method for specific metals leaching into 4% acetic acid solutions at 22^{0}C after a 24h period and the international standard SR EN 12457/1-4 method with distilled water as leaching agent at LSR of 10 l/kg, for 24h period. Amounts of heavy metals have been negligible or non-detectable (iron) in the leaching solutions, being well below the limit values established by the legislation in force.

Keywords: electroplating sludge, pigments, ceramic glaze, stability

Decorative ceramic products are made from inorganic materials with a high content of argil or silicate to which small quantities of other organic materials may be added. These product are shaped and irreversibly transformed and fixed by firing process [1]. The colored glazes are obtained either by the addition of metallic oxides or colored salts which melt into the glaze in order to form colored silicas or by adding colored refractory materials which do not melt but spread evenly in the glaze, transmitting their color. For the use of metallic compounds as pigments in the coloring of ceramic products, it is very important that they are compatible with the glaze and, implicitly, with the firing temperature. Colored pigments are more or less complex metal compounds. Their elements and chemical valence as oxidic compounds in pigments are [2]: Cu (1, 2), Ca (2), Zn (2), Al (3), In (3), Si (4), Sn (4), Pb (2), Ti (3,4), Zr (4), Ce (4), Pr (4), V (4, 5), Sb (3, 4, 5), Cr (3, 6), Mo (4, 6), Mn (2, 4), Fe (2, 3), Co (2), Ni (2) 'i Cd (2). Heavy metals are often derived from heavy industry such as electroplating factories, metal finishing and chemical industry [3]. Removal of heavy metals from industrial liquid and solid waste is essential not only to protect the environment, but also to slow down the fast depletion of heavy metals sources [4]. Considering the issue of environmental protection and natural resource depletion, various alternatives to transform industrial wastes in secondary raw materials are studied [5].

Large amounts of metals are generated in plating industry. The electroplating sludge contains many metallic elements such as Cr, Ni, Fe, Al, Mg, Cu, Pb or Zn. The metal content in electroplatig sludge is high and it is economically viable to extract and recycle them as secondary raw materials in various industries [6]. The heavy metals pollution represents an important global issue because of their extremely toxic effect even at low concentrations [7]. Industrial wastewaters and solid waste contain a high variety of pollutants which depend on industrial activity [8].

There are several methods proposed in literature in order to recover and recycle the electroplating sludge and to reduce its toxicity due to the heavy metals content, such as incorporation/inertization of sludge and implicitly of heavy metals in stable matrices or extraction of valuable components and their use in various industries [9,10]. A possibility of galvanic sludge recovery consists in using of some metal hydroxides/salts extracted from sludge in ceramic products. The remaining cake contains metal traces and it may be eliminated in non-hazardous landfills [11].

This paper presents the results of the research activity in order to etablish the stability and leaching potential of ceramic tiles which have been developed using glazes colored with pigments obtained by the extraction of chromium and iron metals from electroplating sludge. Emissions of toxic substances from the decoration and glaze toxicity have a great importance for hygienic and sanitary conditions of ceramic products. It is mentioned that the use of pigments in non-food products has been pursued.

Experimental part

The heavy metals ions extraction process consisted in the extraction of chromium and iron and zinc by solubilization in order to obtain hydroxides or metal salts with economic value. Thus, the following pigments have been obtained and used in ceramic glazes: green chromium pigment [$Cr(OH)_3$], yellow chromium pigment ($PbCrO_4$), yellow chromium pigment ($BaCrO_4$), red iron pigment [$Fe(OH)_3$] [11,12].

The research has been carried out in order to obtain colored ceramic products by introducing various quantities of chromium and iron pigments extracted from electroplating sludges into white and transparent glaze compositions.

The ceramic body was a fine ceramic mass with a 25% chamotte content, with white colour at firing temperature

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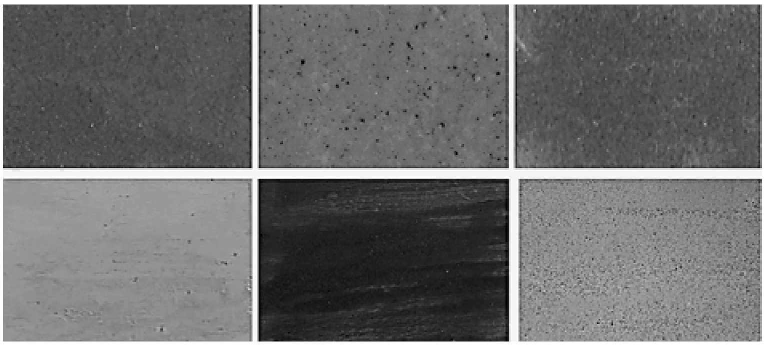

Fig. 1. Ceramic tiles obtained with various concentrations of chromium and iron pigments

of 1070°C. Its firing shrinkage was 3% and water absorption capacity of 9%. Research has been focused on the possibility of obtaining coloured -ceramic products through the use of various amounts of chromium and iron pigments (3%, 5%, 10%) and their addition in vitreous compositions for obtaining colored matte or glossy glazes. The tiles have been fi-red using a predetermined curve of heating and cooling. Some samples are presented in figure 1.

Verification of glaze stability and toxicity was performed by tests for determination of lead and cadmium given off by glazed tiles and leaching tests using distilled water as leaching agent.

The test have been performed for both types of glaze (opaque and transparent), for ceramic tiles without defects as well for those with common defects, and also for the smallest and highest content of pigment introduced into the glazes, namely:

Sample 1 (S1) → opaque glaze with 10% iron pigment $Fe(OH)_3$

Sample 2 (S2) → transparent glaze with 10% iron pigment $Fe(OH)_3$

Sample 3 (S3) → opaque glaze with 3% chromium green pigment $PbCrO_4$

Sample 4 (S4) → transparent glaze with 10% chromium green pigment $PbCrO_4$

Sample 5 (S5) → opaque glaze with 10% chromium green pigment $Cr(OH)_3$

Sample 6 (S6)→ transparent glaze with 10% chromium green pigment $Cr(OH)_3$

Sample 7 (S7) → opaque glaze with 3% chromium yellow pigment $BaCrO_4$

Sample 8 (S8) → transparent glaze with 10% chromium yellow pigment $BaCrO_4$

Determination of stability and toxicity by leaching tests

The leaching tests have been performed according to the international standard SR EN 12457/1-4: Leaching - Compliance test for leaching of granular waste materials and sludges. The procedures described in the European Standard are based on various LSR (liquid–solid ratio) and various particle size. These two parameters play an important role in the process of leaching. In order to carrie out the leaching tests, distilled water has been used as leaching agent. LSR of 10 l/kg has been used. Leaching was carried out with Dissolution Tester for 24 h with continuous slow stirring. The results have been expressed in mg/kg leached dry metter. Results of leaching tests for heavy metals: zinc, total chromium and lead have been compared to the maximum allowable limits for waste acceptance on inert waste landfills in accordance with the requirements of the legislation in force (Order 95/2005).

Determination of lead and cadmium given off by glazed tiles

The lead and cadmium are found in the composition of pigments or glazes, therefore it has been considered necessary to measure the lead and cadmium release from obtained ceramic tiles. Determination of lead and cadmium emission from glazed ceramic tiles has been performed according to the international standard SR ISO 10545-15. Interpretation of the results was carried out in accordance with Article 30, point a) of the Decision no. 1197/2002, as subsequently amended and supplemented, for the approval of the Norms on materials and articles that come into contact with food, the article which states the following limits: 0.8 mg/dm^2 for lead and 0.07 mg/dm^2 for cadmium.

The test has been performed on three identical tiles from each sample. The samples surfaces have been cleaned at about 40^{0}C with liquid household detergent and rinsed with tap water, followed by distilled water and dry in order to avoid stains.

Because the samples that were the subject of the research are flat samples, they were immersed in a vessel containing the test liquid - 4% acetic acid solution. The test has been carried out at a temperature of about 22^{0}C over a 24-hour period. Determination of lead and cadmium emission has been performed from the test solution of each sample by atomic absorption spectrophotometry.

The results have been expressed according to the formula [13]:

$$\rho_A(M) = \rho(M) x \frac{V}{1000} x \frac{1}{A} \quad (1)$$

were:

ρ_A(M) is the extracted metal (Pb or Cd);

ρ(M) is the metal concentration (M) in the extraction solution, determined by prin atomic absorption spectrophotometry, in mg/L;

V is the volume of used test solution/sample;

A is the area of tested surface, in square decimetres.

Results and discussions

Leaching tests with distilled water as leaching agent, LSR of 10 L/kg

The leaching tests has been aim in order to establish if metals are successfully fixed in ceramic tiles and if these are no longer able to migrate into the environment. Leaching tests results for the ceramic samples are presented in table 1.

The results of leaching tests regarding heavy metals: total chromium, lead and zinc,, compared to the maximum admissible limits for acceptance of waste on inert waste landfills, in accordance with the requirements of Order 95/2005, are presented in figures 2-4.

The leaching test result for sample S8-ceramic tile with transparent glaze and 10% chromium yellow pigment $BaCrO_4$, with distilled water, show an amount of total chromium in testing solution higher compared with other samples. For all ceramic samples, the amount of total chromium have been lower compared with the maximum allowable limit established by the legislation in force for inert waste.

Table 1
EXPERIMENTAL RESULTS FOR LEACHING TESTS PERFORMED ON CERAMIC SAMPLES (LSR =10 L/kg)

Ceramic sample	Determined values (LSR =10 l/kg) (mg/kg D.M.*)			
	Total chromium	Lead	Zinc	Total iron
S1	0.2141	0.0011	0.0175	0.0198
S2	0.1699	0.0615	0.0221	0.0152
S3	0.2402	0.0717	0.0233	0.0315
S4	0.1697	0.0364	0.0175	BDL**
S5	0.2191	0.0216	0.0186	0.0058
S6	0.2252	0.0580	0.0186	0.0012
S7	0.3377	0.0285	0.0081	BDL**
S8	0.4312	0.0250	0.0326	0.0227

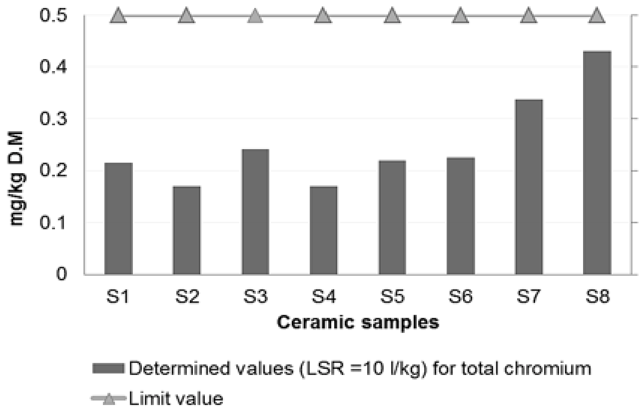

Fig. 2. Leaching tests for ceramic samples - total chromium

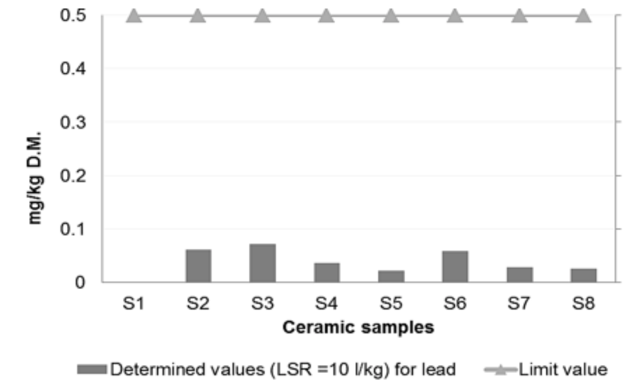

Fig. 3. Leaching tests for ceramic samples - lead

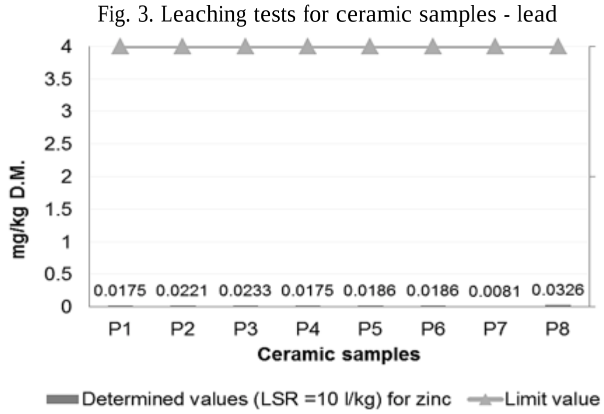

Fig. 4. Leaching tests for ceramic samples - zinc

For all ceramic samples, the amounts of lead and zinc leached in testing solution have been significantly lower compared with the maximum allowable limits established by the legislation in force for inert waste.

It is observed that, according to the results of the leaching tests, the analyzed ceramic samples are safe and non-

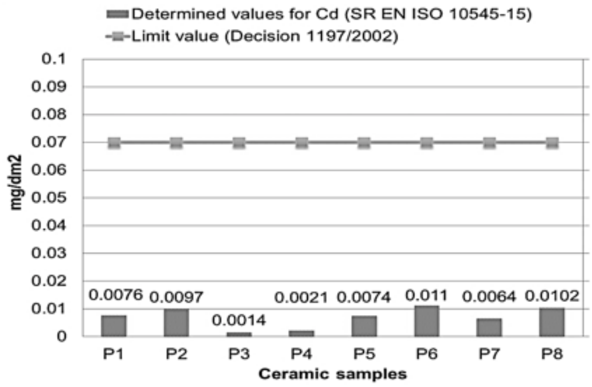

Fig. 5. Cadmium given off by glazed tiles

toxic. The results of leaching test using distilled water as leaching agent indicates a good stability of the analyzed samples and highlight the fact that the metals have been successfully fixed in the vitreous structure of the solidified ceramic glaze.

To enhance the safety of ceramic materials utilization as decorative products, classical leaching tests have been coupled with *determination test of lead and cadmium given off by glazed tiles*. These test is normally applied to household ceramic products.

The results of the lead and cadmium emission test for ceramic tiles samples have been compared to the maximum allowable limits set out in the Decision no. 1197/2002, as subsequently amended and supplemented and they are presented in figures 5 and 6.

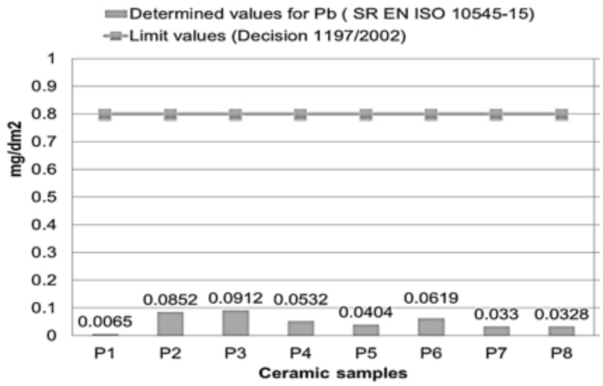

Fig. 6. Lead given off by glazed tiles

By comparing the calculated values for cadmium given off by ceramic tiles samples with the maximum allowable limit of 0.07 mg/dm^2 set out in the Decision no.1197/2002, it is observed that the analyzed ceramic samples were safe and non-toxic, the results being well below the limit set by the law.

Regarding the lead given off by ceramic tiles samples, it is observed that the results are well below the maximum allowable limit of 0.8 mg/dm^2 set by the law.

The obtained results indicate a good stability of the analyzed samples in terms of cadmium and lead emission and highlight the fact that metals have been successfully fixed in the vitreous structure of the solidified ceramic glazes. The calculations of the heavy metal fixation yields in the vitreous structure of ceramic glazes for all samples showed values of over 99.99% fixation yields.

Conclusions

The results obtained on the migration characteristics of heavy metals analysis (Cr, Pb, Zn, Fe, Cd) from the solidified glazed ceramic tiles, by leaching tests, proved the compatibility of the glaze with embedded heavy metals. The results also highlighted a chemical stability of solidified glaze.

The amounts of chromium, lead and zinc leached into the distilled water as testing solution and the amounts of lead and cadmium in 4% acetic acid as testing solution have been significantly lower compared to the maximum allowable limits specified in legislation both for inert waste materials and for ceramic food products.

References

1. *** ED 84/500/EEC, Council Directive of 15 Oct. 1984 on the approximation of the laws of the Member States relating to ceramic articles intended to come into contact with foodstuffs

2. WOLF, E. M., Emaux et glacures ceramiques - Plus de 1100 formules, Deuxieme edition, Edition Eyrolles, Paris, 2010, p. 91

3. KAMAR, F. H., NECHIFOR, A.C., NECHIFOR, G., SALLOMI, M. H., JASEM, A.D., Rev.Chim. (Bucharest), **67**, no.1, 2016, p. 1

4. SIMONESCU, C.M., DIMA, R., FERDES, M., MEGHEA, A., Rev. Chim. (Bucharest), **63**, no.2, 2012, p. 224

5. ANDREOLA, F., BARBIERI, L., BONDIOLI, F., CANNIO, M., FERRARI, A.M., LANCELLOTTI, I., Journal of Hazardous Materials, **156**(1–3), 2008, p. 466

6. GAROLE, D.J., GAROLE, V.J., DALAL, D.S., Research Journal of Chemical Sciences, **2**(3), 2012, p. 61

7. IONESCU, P., RADU, V.M., DEAK, GY., DIACU, E., Rev. Chim. (Bucharest), **65**, no. 9, 2014, p. 1092

8. DEACONU (STANESCU), L.F., Rev.Chim. (Bucharest), **67**, no. 9, 2016, 1728

9. KURNIAWANA, T. A., CHANA, G.Y.S., LOA, W.H., BABELB, S., Chemical Engineering Journal, **118**(1–2), 2006, 83

10. ANDREOLA, F., BARBIERI, L., CANNIO, M., LANCELLOTTI, I., SILIGARDI, C., SORAGNI, E., Physical-chemical Characterization Of A Galvanic Sludge And Its Inertization By Vitrification Using Container Glass, WIT Transactions on Ecology and the Environment, **92**, 2006, p. 23

11. MARCUS, M.I., VLAD, M., MITIU, M.A., Advanced Materials Research, **1143**, 2017, p. 108

12. MARCUS, M.I., VLAD, M., MITIU, M.A., The Annals Of Dunarea De Jos University Of Galati, Fascicle IX Metallurgy And Materials Science, Galati University Press, **2**, 2015, p. 17

13. *** SR EN ISO 10545-15:1999 - Ceramic tiles. Part 15: Determination of lead and cadmium given off by glazed tiles

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