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ECO-TECHNOLOGICAL PROCEDURE OF TREATMENT OF THE SLUDGE GENERATED IN THE GALVANIC WASTE WATER PURIFICITATION

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Abstract. *The subject of the paper is eco-technological procedure of the treatment of the sludge generated during conventional purification (CN^- oxidation, Cr^{6+} reduction, chemical precipitation of the other metals) of the waste water from galvanic process. The detalied analysis of the waste sludge with the determination of high flow (the water eluate) and low flow (HNO_3-eluate) fraction as Cu^{2+}, Cr^{3+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}. The point of the paper is the treatment of the sludge as the dangerous waste into useful product glass-ceramics, with eliminating of the generation of the dangerous and harmful materials in environment.*
Experimental investigation has achived the point and approved that with this procedure it is possible to transform chemical active maters (Cu^{2+}, Cr^{3+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) using the phase and chemical transformation into very stable structure where the polutants can not be activated even under critical conditions as high temperature, influence of acids and alkalies, etc.

Key words: *waste sludge, eco-technological procedure, glass-ceramics.*

1. INTRODUCTORY REMARKS

For many years people have been trying to solve the problem of waste sludge which occurs as a consequence of conventional filtration of wastewater from galvanization (chemical oxidation of cyanide, chemical reduction of chromium (VI) and chemical settling of other metals).

Chemical oxidation of cyanide is usually done with sodiumhypochlorite

$$CN^- + NaOCl \rightleftharpoons CNO^- + NaCl \qquad (1)$$

$$2\,CN^- + 2NaOCl \rightleftharpoons 2NaCl + 2CO_2 + N_2 \qquad (2)$$

$$[Me(CN)_4]^{2-} + NaOCl + 6OH^- \rightleftharpoons Na^+ + Cl^- + 4CNO^- + Me^{2+} + 3H_2O \qquad (3)$$

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Where Me equals Cu, Zn, Cd, Ni.

Towards cyanate ($10-10^3$ times are less toxic than cyanide), carbon (IV) oxide, nitrogen and ions of metals. Chemical reduction of chromium (VI) which is usually done with ferrosulfate in a separate (as well as the oxidation of cyanide) reactor or pool.

$$6Fe^{2+}+Cr_2O_7^{2-}+14H^+ \rightleftharpoons 6Fe^{3+}+2Cr^{3+}+7H_2O \quad (4)$$

Metals (Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Cr^{3+}) usually settle in the form of hydroxide in a base environment (pH≥9) and therefore make waste sludge. The problem of sludge hasn't been solved yet in our country, whereas, in the West, operations and processes that do not result in the occurrence of waste sludge are used. The processes used in the West are the following: electrochemical regenerative processes with unconventional electrodes reverse osmosis, and chemical reduction of sodiumborohydridomile [1,2]. Leaving waste sludge in an open-air place, under the influence of atmospheric rainfalls that have acid pH value, the movement of very toxic and chemically active ions of metals becomes evident according to the following chemism.

$$Cr(OH)_{3\,(S)}+3H^+ \rightarrow Cr^{3+}+3H_2O \quad (5)$$

$$Me(OH)_{2\,(S)}+2H^+ \rightarrow Me^{2+}+2H_2O \quad (6)$$

Where Me equals Cu, Zn, Cd, Ni, Pb itd.

The possibilities of treatment of waste sludge were given [3, 4, 5], however, the suggested eco-technological process more universally and more easily solves the problem of secondary waste materials (sludge, aluminum slag and glass dust), as well as the total protection of environment and obtaining the useful product (glass-ceramics).

2. METHODS OF EXPERIMENTAL RESEARCH

Infrared spectra of waste sludge and glass-ceramics samples were recorded on a FT-IR spectrometer BOMENM (HARTMAN & BRAUN), model BM-Series in the area of wave numbers from 4000 cm^{-1} to 400 cm^{-1} at the resolution of 2 cm^{-1}, using the method of pressed tablets. Potassiumbromide technique for preparing the samples was used for the recording of spectra. The amount of 1 to 2 mg of the examined sample is mixed with 150 g spectroscopically pure KBr (nearly 1% of solid solution). This mixture undergoes vacuumizing and pressing under the pressure of 200 Mpa, out of which the thin permeable pills occur. Referential pills for recording BACKGROUND were made from pure KBr. ESR or EPR spectra of waste sludge and glass-ceramics samples were recorded on ESR spectrometer BRUKER ER 200 D, with the range of magnetic field of 0-9 kG, modulation of 100 kHz, and working frequency of klystrons of 9,3 GHz and microwave power of 13 mW. Measurements were carried out on finely fitted samples in quartz test tubes with the outer diameter of 4mm and the inner one of 3 mm.

For the determination of the concentration of metals in low-flow and high-flow fractions of waste sludge, atomic absorbers (PERKIN ELMER AAM1100 AND VARIAN AA-20) were used. Differentially thermic analysis (DTA), thermogravimetric (TG) and differentially thermogravimetric (DTG) analyses were carried out on a "Derivatograph" 1500, the possession of MOM firm from Budapest.

For the accomplishment of eco-technological procedure of treatment of waste sludge, mechanical (grinding and milling on a colloid mill) and thermochemical methods were used.

3. SURVEY AND DISCUSSION OF THE RESULTS OF EXPERIMENTAL RESEARCH

Ecological risk of waste sludge is determined on the basis of defining the value of high-flow and low-flow fractions of series of metals by a standard procedure - U.S. EPA 1997/222. The primary ecological risk of waste sludge was being determined on the basis of rinsing the representative samples in distilled water and on the basis of the analysis of metal. In the results a term-water-eluate has been adopted for this movable fraction. For the sake of a more detailed insight into the pollution potential, and at the same time having in mind the chemical origin of waste sludge, a low-flow fraction was also determined, which is more strongly bonded and thus stands for the pollutant tank. Low-flow metal fraction was isolated, also, by a standardized procedure of rinsing with the diluted nitric acid. This fraction is marked as HNO_3-eluate. Criteria, according to which the comparation of concentration of metal in water after rinsing the representative samples of waste sludge was carried out, are taken from Holland list 8935/1998, which had been adopted by European Community. These results are shown in table number 1.

Table 1. Comparation of hifh-flow (H_2O-eluate) and low-flow (HNO_3-eluate) fractions of metals in representative samples of waste sludge, with standard values given in Holland list 8935/1998: A - reference value for standard underground water; B - concentration at which more detalied investigation and protection is advised (regulation of EEC)

Pollutant	H_2O-eluate (mg/dm^3)	HNO_3-eluate (mg/dm^3)	A (mg/dm^3)	B (mg/dm^3)	Unfulfilment of criteria
Cu	0,137	106,1	0,015	0,050	A, B
Zn	0,269	1222	0,150	0,200	A, B
Ci	9,56	977	0,001	0,050	A, B
Ni	1,935	1210	0,015	0,050	A, B
Cd	2,839	1203	0,005	0,050	A, B
Pb	0,000	9,585	0,005	0,050	A, B

Eco-technological procedure of treatment of waste sludge is modeled in the form of a logical scheme block in figure 1. Also, chemical and physio-chemical analyses, which confirm the transmission of dangerous and toxic materials from the sludge into chemically stable structure, into the product glass-ceramics, are given.

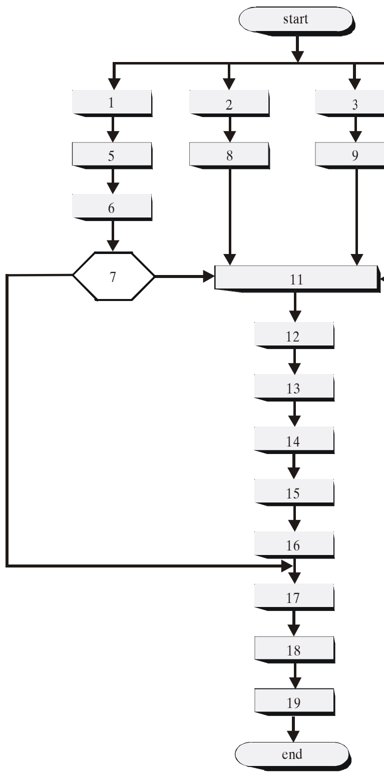

Fig. 1. Eco-technological procedure of treatment of the galvanic sludge

1. representative sample of waste sludge
2. aluminum slag
3. waste glass
4. flux B_2O_3
5. drying of waste sludge
6. grinding and milling the sludge on a colloid mill
7. determination of concentration of metal in sludge by use of AAS
8. grinding and milling the waste aluminum slag on a colloid mill
9. grinding and milling the waste glass on a colloid mill
10. milling B_2O_3 on a colloid mill
11. preparation and homogenization of mixture for the synthesis of glass-ceramics
12. pouring the homogenized mixture into the mold for melting
13. putting the mold with homogenized mixture into blast furnace (800-1200^{o}C)
14. melting the mixture and checking if content is in a liquid state
15. casting the molten content into preheated graphite mold (glass-ceramics)
16. FT-IR analysis of sludge and glass-ceramics
17. ESR and EPR analysis of sludge and glass-ceramics
18. DTA, TG, DTG and T analysis of glass-ceramics
19. Conclusions with the suggestion for solving the problem

Confirmation of the efficiency of the eco-technological procedure of treatment of sludge into glass-ceramics was carried out by use of FT-IR spectrophotometry and EPR or ESR spectroscopy. In addition to that, some chemical and phase transformations have been confirmed by uniting the dangerous and toxic metals with aluminosilicate phase in the form of solid solutions. IR spectrum of the obtained glass-ceramics is shown in figure 2.

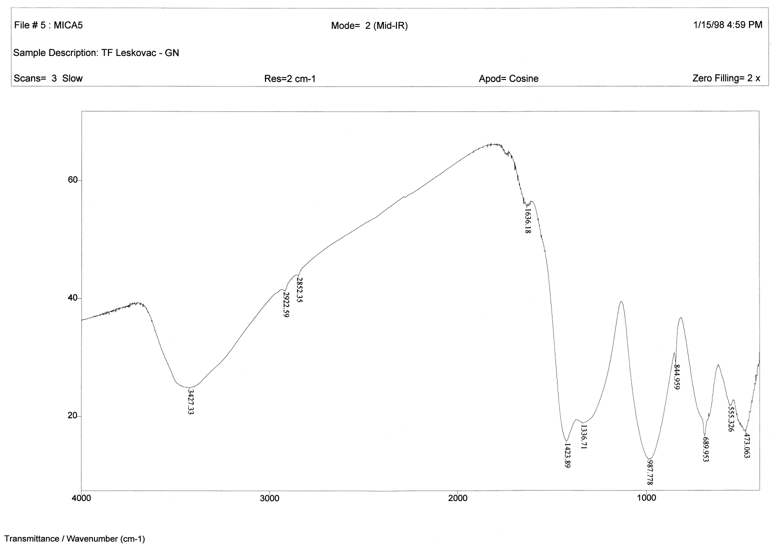

Fig. 2. IR specttrum of glass-ceramics

On the basis of IR spectrum, the structure of glass-ceramics was confirmed by the line in the area from 555 to 987 cm^{-1}, which shows us the dominant amount of aluminosilicate in the form of $Al_2O_3 \cdot SiO_2 \cdot 2H_2O$. The lines in the area from 473 to 844 cm^{-1} show us the incorporation of metal in the form of solid solutions (Cr_2O_3, $CuTiO_3$). ESR spectrum of glass-ceramics is shown in figure 3.

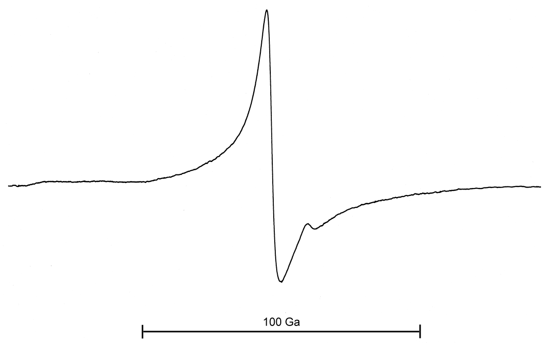

Fig. 3. ESR specttrum of glass-ceramics

The sample was recorded under the following values of spectrometer:
– Gaining (GAIN), G=8,0-10^4;
– Attenuation, AT=13;
– Speed of tracing, ST=500 sec;
– Width of the field, SW=2-10^3 Ga;
– Center of the magnetic field, CF=1650 Ga and
– Modulation, MOD=10-1.

ESR spectrum of glass-ceramics has got a defined signal at the low value of the magnetic field of 1650 Ga which can be explained by the total reducing (below 1%) of paramagnetic metals during the treatment and by their uniting with the aluminosilicate phase of glass-ceramics. DTA, TG, DTG and T curves of glass-ceramics are shown in figure 4.

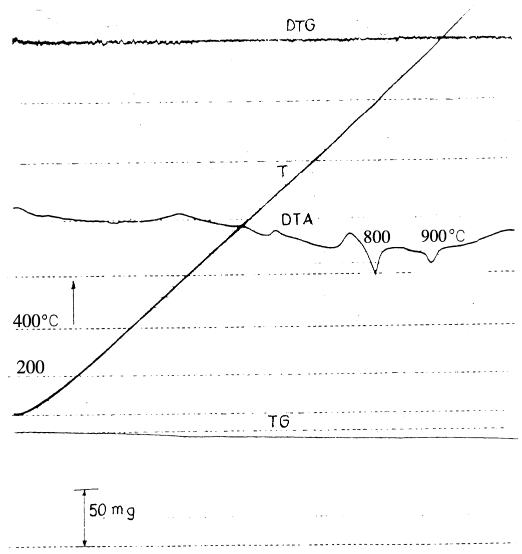

Fig. 4. DTA, TG, DTG i T curve of glass-ceramics

The curves are obtained under the following conditions:
– Weight of the sample - 310 mg;
– TG sensitivity 200 mg;
– DTA 1/10 mV;
– DTG 1/10 mV;
– T max 1200°C;
– Speed of heating 10°/min;
– Atmosphere - air.

According to figure 4 it can be seen that up to the temperature of 600°C there are no transformations happening in the examined glass-ceramics. During further heating about 5 mg of the weight of the sample is being lost. At the temperature of 800 and 900°C some clearly defined endothermic transformations are happening, the second of which is - melting the examined material.

4. CONCLUSION

On the basis of the experimental research and also on the basis of results shown and discussed, the following conclusions can be drawn:

The ecological risk was determined in putting aside galvanic waste sludge by use of standard procedure and by determining low and high flow fractions of metal.

The criteria according to which the comparison of concentration of metal in water after rinsing the representative samples of waste sludge was carried out have been taken from Holland list 8935/1998, which had been adopted by European Community. From table number 1 can be concluded that there was the unfulfilment of criteria by all the examined metals except by lead in water eluate.

The main hypothesis, which states that the chemical activity of waste sludge should be controlled and directed towards obtaining the useful product (glass-ceramics), has been experimentally confirmed Controlling and directing the chemical activity can be achieved by use of eco-technological procedure of treatment. Moreover, the hypothesis confirmed that spontaneous and long-lasting processes in sludge that is in contact with living environment should not be allowed.

The efficiency of the eco-technological procedure of treatment of waste sludge into ceramics FT-IR was exactly confirmed by spectrophotometry. At the same time chemical and phase transformations were confirmed by uniting dangerous toxic substances (Cr, Cu, Cd etc.) with aluminosilicate phase in the form of solid solutions.

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EKO-TEHNOLOŠKI POSTUPAK PRERADE MULJA NASTALOG PREČIŠĆAVANJEM GALVANSKIH OTPADNIH VODA

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Predmet rada je eko-tehnološki postupak prerade mulja nastalog konvencionalnim prečišćavanjem (oksidacijom CN^-, redukcijom Cr^{6+}, hemijskom precipitacijom ostalih metala) otpadnih voda procesa galvanizacije. U radu je detaljno analiziran otpadni mulj određivanjem lako (vodeni eluat) i teže (HNO_3 eluat) pokretljive frakcije kao što su Cu^{2+}, Cr^{3+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}.

Cilj rada je prerada mulja kao opasnog otpada u koristan proizvod staklo-keramika, uz eliminisanje opasnih i štetnih materija u životnoj sredini.

Eksperimentalna istraživanja su ostvarila cilj i potvrdila da se ovim postupkom hemijski aktivne materije (Cu^{2+}, Cr^{3+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) mogu prevesti faznim i hemijskim transformacijama u izuzetno stabilnu strukturu gde se polutanti ne mogu pokrenuti i pod kritičnim uslovima kao što su visoka temperarura, dejstvo kiselina i baza i slično.

Ključne reči: *otpadni mulj, eko-tehnološki postupak, staklo-keramika.*