UNIVERSITY OF NIŠ
The scientific journal **FACTA UNIVERSITATIS**
Series: **Working and Living Environmental Protection** Vol. 1, No 4, 1999, pp. 91 - 100
Editor of series: Ljiljana Rašković, e-mail: ral@junis.ni.ac.yu
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NEW ECO-TECHNOLOGICAL PROCEDURE OF THE PROCESS OF TREATMENT OF ALUMINIUM SLAG GENERATED BY MELTING AND CASTING OF ALUMINIUM AND IT'S ALLOYS

UDC 628.47.045

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Abstract. *This paper represent the part of much larger research of the treatment of aluminium slag which is defined as the dangerous waste according to Yugoslav and international regulations. Untreated aluminium slag is contaminating environment (water, air and earth) by emission of liquid and gaseous phases of dangerous maters. Experimental investigation shown in this paper are representing new technology of treatment of aluminium slag by converting it into the useful products and eliminating generation of dangerous and harmful maters. Efficiency of eco-technological procedure is approved by modern fundamental methods of chemical and physico-chemical analyze. It is obtained glass-ceramic characterized by large contents of alumo-silicates and the structure of it is approved. Such a new eco-technological procedure of the process of treatment of aluminium slag is enabling complete protection of environment together with using slag as secondary raw material. This is in accordance with the recent trends in recycling and regeneration of waste.*

Key words: *aluminium slag, glass-ceramic, eco-technological procecdure*

INTRODUCTION

Industrial waste that is toxic, reactive, self-inflammable and corrosive, is called dangerous waste. Chemical composition of the waste that make it dangerous is strictly defined by the law regulations in particular countries. In our country chemical composition is defined by "Regulations on the way of treating the waste with characteristics of dangerous matters", according to which the slag arising with melting and casting of aluminium and it's alloys is dangerous waste because it contain inorganic compounds of fluor, copper, zinc, beryllium, chromium and the other metals. Aluminium

Received November 23, 1999

slag is treated as dangerous waste according to standards ISO/TC 207 and ISO/TC 200. Beside great toxicity slag is arising in meaningful quantities that is 50-70 kg per tone of refined aluminium. On the area of SR Yugoslavia, under normal conditions of productions, aluminium slag is arising at quantities of 10.000 tones per year. the problem of slag is not comprehensively solved, as at it's deponing toxic gases are released (HF, HCl, H_2S, PH_3, etc.) and that is becoming constant source of environment pollution.

The subject of this paper is eco-technological procedure of the process of treatment of aluminium slag as the dangerous waste into the useful products (salts that are regenerated and turning back into the technological process of aluminium and it's alloys casting, aluminium sulphate that are often used as coagulant in water purification and glass ceramics for wide applicationsć.

The point of this paper is processing of aluminium slag as dangerous waste into useful products connected with eliminating of harmful and dangerous matters in environment.

The basic hypothesis is that slag has a great chemical activity as well as great number of active constituents and ingredients. Starting from basic hypothesis, activity of slag should be controlled and directed to obtaining of useful products by certain technological procedures and to prevent spontaneous and lengthy processes in slag in contact with environment-earth, water and air.

2. METHODS AND MATERIALS OF EXPERIMENTAL INVESTIGATION

For analyzing of aluminium slag as well as for monitoring of transforming of chemically active matters from slag into chemically stable matters and useful products, modern methods for chemical and physico-chemical analyze have been used as: Fouries transformation of infra red spectroscopy (FT-IR), electron-spin resonance (ESR) or electron-paramagnetic resonance (EPR) and atomic absorbance spectrophotometry (AAS).

Infra red spectrum of the samples of aluminium slag, intermediate aluminate (partially treated aluminium slag) and glass-ceramic (completely treated aluminium slag) are made on FT-IR spectrophotometer BOMEM (Hartman & Braun), model MB-Series in the range of wave numbers from 4000 cm^{-1} to 400 cm^{-1}, and resolution of 2 cm^{-1}, according to method of pressed pellets. For recording of spectra kalium-bromid (KBr) technique for samples preparing has been used. Quantity of 1-2 mg of spectroscopy pure KBr (nearly 1% solid solution). Mix is vacuumed and pressed under pressure of 200 MPa giving thin transparent pellets. Reference pellet for recording of BACKGROUND is prepared of pure KBr.

ESR or EPR spectra of the samples of aluminium slag, intermediate aluminate (partially treated aluminium slag) and glass-ceramic (completely treated aluminium slag) are recorded on ESR spectrometer BRUKER ER200D, with the range of magnetic field of 0-9 kG, modulation of 100 kHz, working frequency of klystron 9.3 GHz and microwave strength of 13 mW. Measuring have been done of fine crushed samples in quartz cuvette with outside diameter of 4 mm and inner one of 3mm.

Determination of metal concentration in high flowing and low flowing fraction of aluminium slag has been done using atomic absorption spectrophotometry on atomic absorber PERKIN ELMER AA M1100.

For realization of eco-technological solution of aluminium slag processing into useful products (glass-ceramic, aluminium sulphate and regenerated salts for refining and degassing) are used mechanical (breaking and grinding on colloid mill), physico-chemical (evaporation, crystallization) and thermochemical (melting) methods.

Basic material that is used in this investigation is waste aluminium slag, which represent dangerous waste, as it contain inorganic compounds of fluor, beryllium, copper, zinc, chromium and many other metals. Eight representative samples of aluminium slag has been prepared that represent balanced mix of larger number of instantaneous samples taken during defined time interval (1-24h). Also, representative samples are prepared from technological production processes in factories "Nissal"-Niš and "Valjaonica aluminijuma"-Sevojno. Technological processes were included next types of alloys: Al-Mg-Si, Al-Si, Al-Mg, Al-Si-Mg-Mn, Al-Cu, Al-Zn, Al-Si-Cu-Mg-Ti, Al-Si-Cu-Fe, Al-Si-Cu, Al-Mn-Cu and Al-Cu-Mg-Mn-Si. Salts for refining and degassing that are used and are contained in representative samples of slag are imported, with different quantitative ratio but qualitatively they contain: NaF, NaCl, Na_3AlF_6, AlF_3, $MgCl_2$, MgF_2, KBF_4, K_2SiF_6, K_2TiF_6, CaF_2 and LiCl.

Another material used for producing glass-ceramic and binding of toxic matters from aluminium slag is waste glass from factory "Nissal" from Niš. Average composition of used waste glass shown in mass percentage is: 76% SiO_2, 11%PbO, 8% ZnO, 2% B_2O_3, 2% BaO and 1% ZrO_2. Waste glass of defined composition is prepared for synthesis of glass-ceramic by breaking followed by fine grinding on colloid mill.

Except waste materials used in this experimental investigation pure substances have also been used: B_2O_3 (as melting agent for synthesis of glass-ceramic), NaOH (for transformation of Al_2O_3 into AlO_2^-), H_2SO_4 (for synthesis of $Al_2(SO_4)_3 \times xH_2O$) and distilled water.

3. Results and discussion

New eco-technological procedure of the process treatment of aluminium slag as the dangerous waste into useful products (regenerated salts for refining and degassing that are turning back into technological process of melting and casting of aluminium and it's alloys; aluminium sulphate that is used in water purification by the process of coagulation; glass-ceramic that could widespread be used because of it's thermal, chemical and mechanical resistance) has been given as the model in the logical block scheme in the Fig. 1. Also, results of chemical and physico-chemical analyzes are given which approve transforming of chemically active (dangerous) matters from slag into chemically more complex and stable structure-glass-ceramic product.

1. Preparing of the representative sample of waste aluminium slag;
   - separation of metal aluminium from nonmetal compounds
   - fine milling of the slag and homogenization of representative sample
2. Separation of the sample of slag in two parts;
3. Analyze of the chemical composition of the slag (AAS, Ion selective analyze, UV VIS spectrophotometry and argentometry);
4. Determination of low-flow fraction (according to U. S. EPA 1997/222);

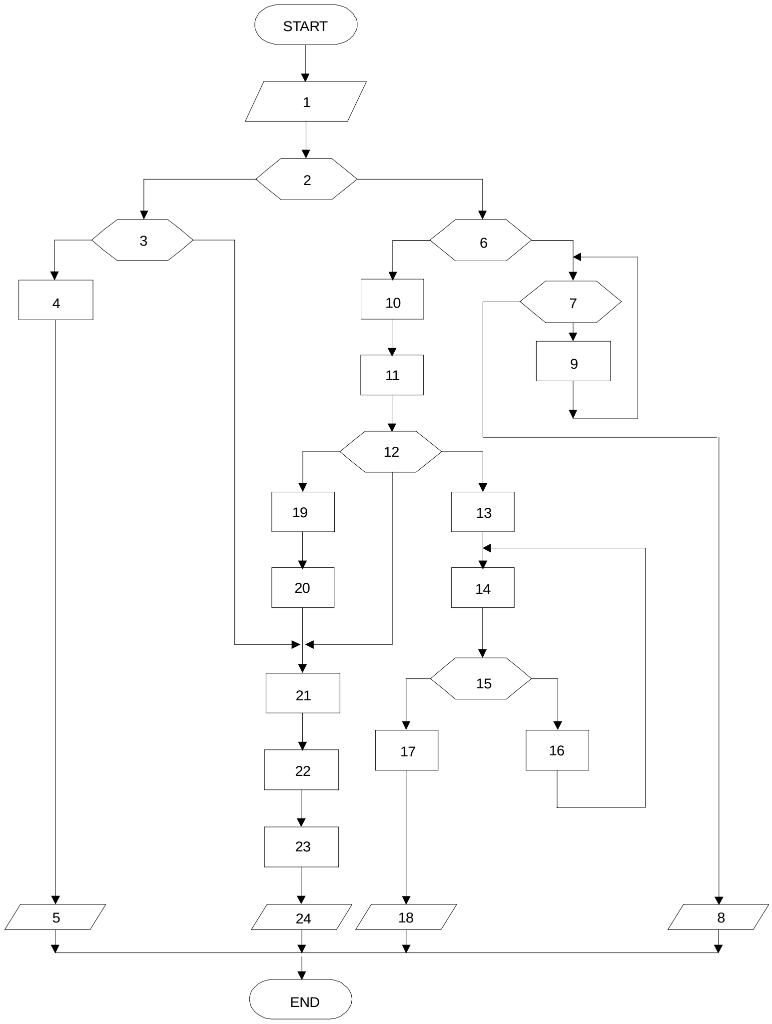

Fig. 1. New eco-technological procedure of the process of treatment of aluminium slag into the useful products

5. Analyze of the chemical composition of low-flow fraction (AAS, Ion selective analyze, UV VIS spectrophotometry and argentometry);
6. Chemical dissolution of soluble salts and separation of non-soluble deposits from filtrate;
7. Chemical-technological treatment of filtrate (evaporation and crystallization) with regeneration of salts that are returning to technological process of melting aluminium and it's alloys;
8. Regenerated salts that are returning back to technological process of melting and casting of aluminium after correction of composition (product I);

9. Returning of rest water to evaporation and crystallization as to complete regeneration of the salts, with afterward chemical analyze of the rest water;
10. Drying of non-soluble deposit based on hydroxide and oxides of metal;
11. Analyze of chemical composition of non-soluble deposit (AAS);
12. Melting of non-soluble deposit with NaOH ;
13. Treatment of the generated black suspension with H_2SO_4;
14. Evaporation of generated solution until the presence of first crystals of $Al_2(SO_4)_3$;
15. Filtration and drying of generated salts based on $Al_2(SO_4)_3$;
16. Returning of filtrate to evaporation;
17. Analyze of chemical composition generated salt based on $Al_2(SO_4)_3$;
18. Generation of $Al_2(SO_4)_3$, $NaAl(SO_4)_2$ and $KAl(SO_4)_2$ (product II) that could be used as coagulation agents for treatment of water;
19. Preparing of non-soluble deposit for synthesis of glass-ceramic by mixing it with dust of waste glass with addition of melting agent (borax);
20. Melting of mix and transferring to graphite cast as to make glass-ceramic (product III);

22 and 23. IR, DTA, DTG, EPR and ESR analyzes of the slag, intermediaries, and glass-ceramic;

24. Conclusions with solution of the problem.

Infra-red spectrum of homogenized representative sample of aluminium slag is shown on Fig. 2.

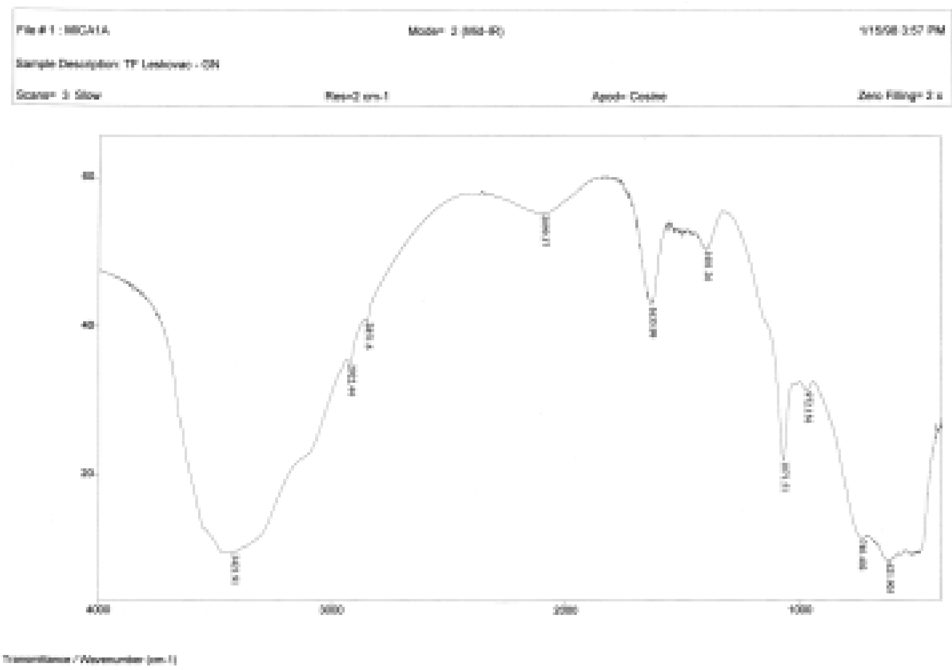

Fig. 2. IR-spectrum of representative sample of aluminium slag (sample 1)

On the basis of IR-spectrum of aluminium slag that is shown on the Fig. 2. (sample 1) it can be concluded that the slag represent complex composite of different metal oxides. Water of crystallization in the structure of these oxides is characterized by valent vibrations of hydroxyl group on the 3421 cm^{-1}, in which width and the shape of the band is pointing out formation of relatively weak hydrogen bonds (about 25 $kJmol^{-1}$). Hydroxyl group is, also, characterized by the band in deformational region on 1635 cm^{-1}.

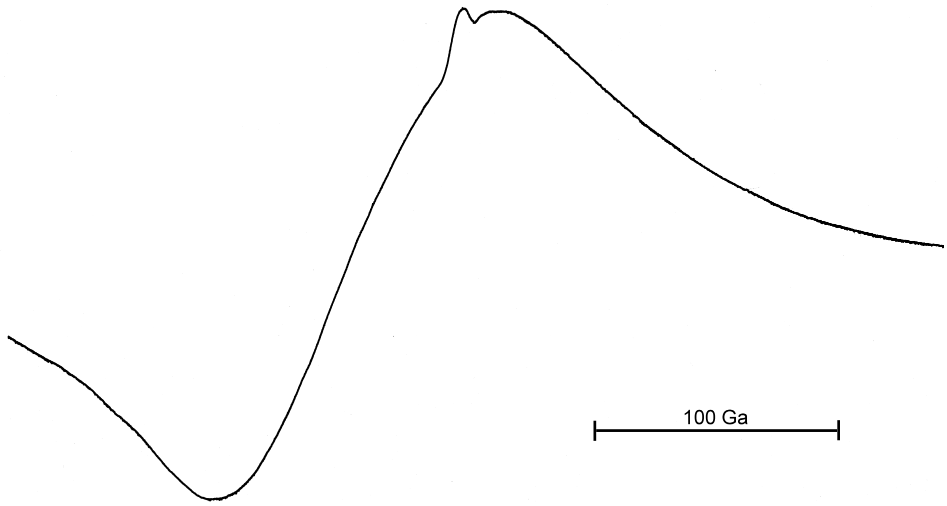

Fig. 3. ESR spectrum of representative sample of aluminium slag (sample 1).
GAIN, $G = 25 \times 10^3$; AT = 13; ST = 500 sek; SW = 4×10^3Ga; CF = 3495Ga; MOD=10×1

In the sample 1 (Fig. 2.) dominant in the content Al_2O_3 has been determined on the basis of the band in the region of 500 to 900 cm^{-1}. Also, in the sample 1 the presence of alumo-silicates in small percentage is determined. Identification is hard because of overlapping the band caused by the presence of hydroxyl group, but on the base of the band on 1070 cm^{-1} it can be concluded that silicates in the form with water of crystallization $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ are present. Also, on the basis of spectral structural correlation (comparison with known IR spectra) relatively weak intensity band in the IR spectrum of the sample 1 could be seen on about 420 cm^{-1} caused by valent Fe-O vibrations.

On the Fig. 3. ESR spectrum of representative sample of aluminium slag (sample 1) is shown on which previous analyzes of AAS and FT-IR spectroscopy.

Very wide line (over 500 G) in the spectrum of the sample 1, that is shown in Fig. 3, is caused by high concentration (over 5%) of paramagnetic toxic ions (Cu^{2+}, Mn^{2+}, Fe^{3+}, Ti^{2+}, Ti^{3+}, etc.) and by their high chemical activity in the sample giving strong spin-spin interactions because of relatively short inter-atomic distance.

Further investigations have had a pint in complete binding of dangerous and harmful matters from aluminium slag into product with practical application as glass-ceramic using waste glass and melting agent (B_2O_3). Eco-technological procedure of producing glass-ceramic from aluminium slag and waste glass is shown in Fig. 1. Confirmation of produced structure of glass-ceramic as well as of the way of chemical bonding of harmful matters that guarantee their low chemical activity is made by IR and ESR spectra of synthesized glass-ceramic.

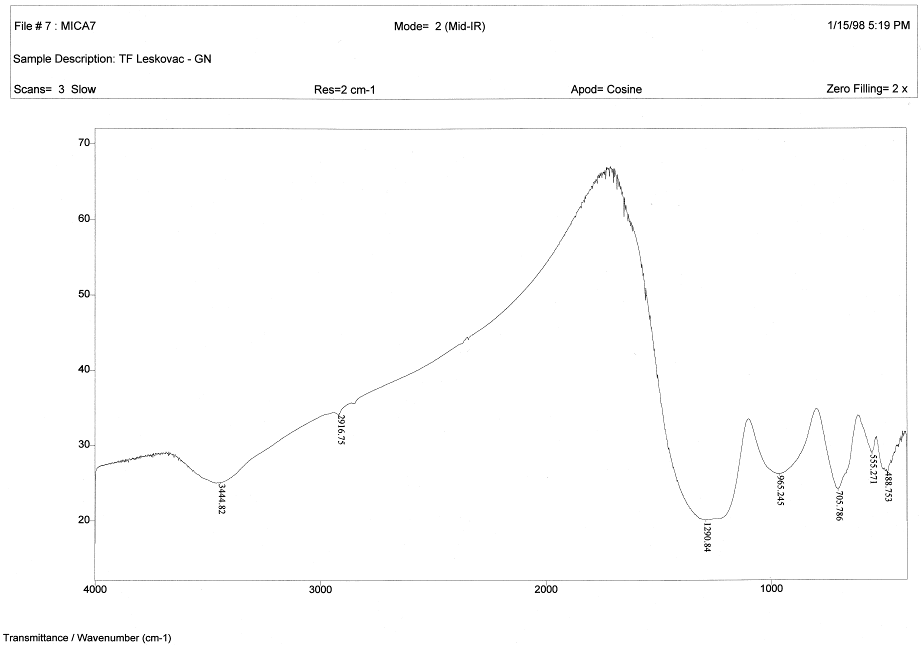

Fig. 4. IR-spectrum of glass-ceramic (sample 2)

In Fig. 4. IR spectrum of glass-ceramic produced from representative sample of aluminium slag (sample 1) is shown.

In the sample 2 of glass-ceramic in IR spectrum bands on 560 and 660 cm^{-1} are pointing out presence of the chromium oxide (Cr_2O_3). Exactly these bands are showing that very toxic chromium is bonded as oxide to silicate phase and is completely chemically inert. Except detoxification of chromium, glass-ceramic is adopting esthetical value as Cr_2O_3 is well known pigment giving very nice color.

Stronger by intensity and shape the band in the region from 600 to 800 cm^{-1} is confirming presence of silicate phase with dominant content of alumo-silicates in the form of $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ as well as magnesium-aluminium-silicate with chemical formula $Mg_2Al_4Si_5O_{18} \cdot xH_2O$. Also, in the sample 2 it is obvious elimination of water of crystallization during melting on the high temperature as the band on 1630 cm^{-1} is missing. Dominant presence of copper (II) titanate (IV) ($CuTiO_3$), is confirmed by the shape and intensity of the bands in the region from 400 to 800 cm^{-1}. Exactly the bands in this region (400-800 cm^{-1}) are approving transformation of very toxic copper and titanium that are bonded in oxides as solid solutions and are completely chemically inert which is very important from the point of environment protection. As the chromium-oxide, as well as the copper and titanium oxides, are well known pigments, and that is giving to glass-ceramic higher esthetic value during casting into different shapes.

Confirmation of the efficiency of eco-technological procedure of the treatment of aluminium slag is given by ESR-spectrum of glass-ceramic (sample 2) shown in Fig. 5.

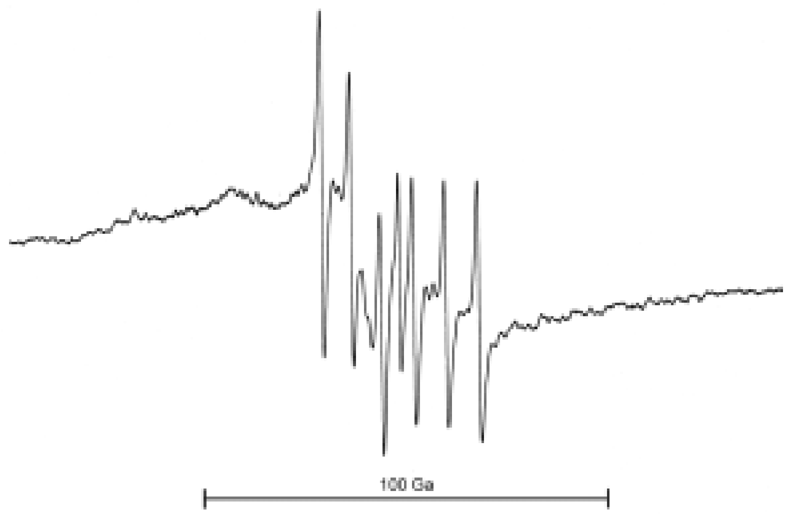

Fig. 5. ESR-spectrum of glass-ceramic (sample 2).
The spectrum is recorded at next values of spectrometer: GAIN, G = 3,2 × 105; AT = 13; ST = 500 sek; SW = 2 × 103Ga; CF = 3490Ga; MOD = 10 × 1.

Differently from the sample of aluminium slag in the beginning (sample 1) defined ESR-spectrum is recorded for glass-ceramic (sample 2) indicating that there are no more strong spin-spin interactions and lowering of the concentrations of toxic paramagnetic metals is happened. Characteristic sextet of the lines in Fig. 5. is indicating low concentration of Mn^{2+} ions where the value of spectral parameter which is defining the position of principal line g = 2.0 and constant of hyperfine splitting for unpaired electron that is localized on the atom with nuclear spin *a* = 80 Ga.

ESR spectrum is indicating lowering of concentrations of toxic paramagnetic metals approving efficiency of eco-technological procedure of transformations. IR-spectroscopy of the same samples (1 and 2) is indicating the way of chemical bonding that guarantee low chemical activity of toxic metals. Also, confirmation of alumo-silicate phases in IR spectrum is approving that the synthesis of glass-ceramic has happened.

4. CONCLUSION

On the basis of experimental investigation as well as on the basis of shown and considered results next conclusions were made:

1. The basic hypothesis that aluminium slag has a great chemical activity and great number of active constituents is approved. A number of dangerous and harmful

maters as: copper, chromium, titanium, beryllium, fluorides, etc. is approved by chemical analyze (AAS, ion-selective analyze for fluor, ESR, FT-IR).

2. Experimentally is approved the main hypothesis that chemical activity of aluminium slag should be controlled and directed to producing of useful products through application of certain eco-technological procedures of treatment and not to allow spontaneous and long term processes in slag in contact with the environment-earth, water and air.
3. Using eco-technological procedure of processing of aluminium slag into glass-ceramic complete protection of environment is achieved and, in the same time, the useful product is produced without generating of new waste. The reason for that is transformation of dangerous and harmful matters (Cr, Cu, Ti, Be, F, Mn, etc.) into state of low chemical activity by phase and chemical transformations. Metals, evaporating and insoluble fluorides are incorporated into structure of alumo-silicate phase in glass-ceramic in the form of solid solutions, as stable compounds. Fluor from soluble compound of natrium, kalium, magnesium, aluminium is regenerated in the form of the same salts that are turning back to technological process of melting and casting of aluminium and its alloys (Fig. 3. 1.).
4. Efficiency of eco-technological procedure of processing of aluminium into glass-ceramic is approved by FT-IR spectrophotometry and ESR-spectroscopy. Also, chemical and phase transformations are approved connected with bonding of dangerous and harmful matters (Cr, Cu, Ti, Be, etc.) to alumo-silicate phase in the form of solid solutions.

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NOVI EKO-TEHNOLOŠKI POSTUPAK PROCESA PRERADE ALUMINIJUMSKE ŠLJAKE NASTALE TOPLJENJEM I LIVENJEM ALUMINIJUMA I NJEGOVIH LEGURA

Miodrag P. Stanisavljević

Ovaj rad predstavlja deo mnogo obimnijeg istraživanja prerade aluminijumske šljake, koja se prema našim i svetskim kriterijumima svrstava u grupu opasnog otpada. Neprerađena aluminijumska šljaka vrši sveobuhvatno zagađivanje životne sredine (vode, vazduha i tla) emisijom tečnih i gasovitih faza opasnih materija.

Eksperimentalna istraživanja prezentirana u ovom radu prikazuju novu tehnologiju prerade aluminijumske šljake u korisne proizvode uz eliminisanje pojave opasnih i štetnih materija u životnoj sredini. Efikasnost eko-tehnološkog postupka je egzaktno dokazana najsavremenijim *fundamentalnim metodama hemijske i fizičko-hemijske analize. Dobijena je staklo-keramika koju karakteriše visok sadržaj alumo-silikata i njena struktura je potvrđena. Ovakav novi eko-tehnološki postupak prerade aluminijumske šljake omogućava potpunu zaštitu životne sredine uz korišćenje šljake kao sekundarne sirovine, što u potpunosti poštuje savremene tendencije reciklaže i regeneracije otpada.*

Ključne reči: *aluminijumska šljaka, staklo-keramika, eko-tehnološki postupak*