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Solid waste management

COMBINED METHOD FOR UTILISATION OF INDUSTRIAL WASTE PRODUCT

D. Y. BOJINOVA

University of Chemical Technology and Metallurgy, 8 Kliment Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: bojinova@uctm.edu

Abstract. A subject of the investigation is a waste product resulting from copper ore flotation of the company "Medet" ore deposit. The waste contains a number of valuable elements but they can not be extracted by a process of direct acid degradation even after a thermal treatment. Acid extraction of the useful compounds from Al-containing industrial waste product (IWP) after its preliminary mechanical activation were investigated. The kinetics of acid decomposition of mechanically activated industrial waste product (MAIWP) at different time of mechanical activation and temperatures with H_2SO_4 (50% w/w) through regression analysis has been studied. The mechanical activation has been done in a planetary mill of "Pulverisite 5" type. The duration of activation was 2, 4, 6, 8 and 10 h, respectively. The degradation process of Al-containing IWP was examined for the extraction of Al, K, Na, Mg, Ca, Zn and Mn. On the basis of the obtained results, the extent of the total degree of extraction of the controlled tested elements was determined as percentage compared to their content in the initial IWP. Based of the experimental data, adequate regression equations were deduced and the optimum conditions were determined.

Keywords: aluminosilicates, acid extraction, Al-contained industrial waste product, decomposition of aluminosilicates, mechanical activation.

AIMS AND BACKRGOUD

The continuous increase in the aluminium consumption and the limited store of high quality bauxites explain the interest towards new ways for enlargement of the sources for Al_2O_3 and aluminates production. In this respect aluminium containing raw materials are prospective (nephelines, kaolins, clays, alunites, leucites) as well as industrial wastes[1-3]. There are many minerals in the crust of the earth containing aluminium, but because of lack of appropriate technologies for their processing it makes them industrially useless. The diversity of mineral forms where aluminium could be found and the various content of the other components pose the difficult task for development of effective methods for their extraction. Many nonbauxite raw materials are complex. Along with Al_2O_3 they contain K_2O, Na_2O, etc. that makes their processing more complicated. Nevertheless, their processing could be profitable when more effective schemes are applied.

During the enrichment of copper ore a waste (IWP) comes off with a constant chemical composition that does not require additional mechanical treatment. The rather high SiO_2 content and relatively low content of useful components ($Al_2O_3+K_2O+Na_2O=24$-25% w/w) set limits to the application of the alkaline caking method for its treatment. Besides Al_2O_3 in the IWP presents an non-acid dissolved form. Complex schemes for such type of raw materials are developed thus requiring rather complicated both technological and equipment mounting because of the complexity in the mineral and chemical composition of the processed raw materials. Despite their insufficiency, these methods pose a final decision of the difficult question for the production of pure ferric aluminium salts.

A combine sulphuric acid method for complex processing of nepheline concentrate was developed[4-6]. The method consists in sulphatation of the concentrate through caking with sulphuric acid, extraction of the sulphate mass using circulating solutions, separation of liquid and solid phases, evaporation of the sulphate solution with alum separation, decomposition of alums to aluminates through reduction and next processing by known methods to Al_2O_3 and alkaline salts.

According to combine sulphuric acid-alkaline method[7] for treatment of aluminium containing nonbauxite raw materials, the cake after sulphatising caking is extracted with NaOH. Aluminium hydroxide is settled from the solution by usual methods followed up with red-hot-making to Al_2O_3.

Investigations were done on "Medet's steril" (IWP) using combine alkaline method[8]. The process consists in preliminary flotation followed up by alkaline autoclave treatment. From the alkaline solutions sodium metasilicate, calcium metasilicate and carbonised calcium metasilicate are produced. The chemically enriched concentrate is treated according to the method of alkaline caking with lime to produce Al_2O_3, K_2SO_4 KOH and slime for Portland cement thus deriving up to 86% Al_2O_3 and 95% of alkaline materials. It was established the possibility for decomposition of partially or completely acid nondissolved nonbauxite Al-containing raw materials and deriving of Al_2O_3 and other useful components through thermal treatment of their mixtures with natural phosphate followed by acid leaching of the obtained cakes[9].

There are some data in literature[10-14] about the application of the mechanical activation method to different types of aluminosilicates for determination of the physic chemical changes that occur to them. The investigations confirm that complicated processes occur as a result of the mechanical activation. They are concerned with the aluminosilicates crystal lattice and an appearance of "active" sites in their structure. Our investigations present a combine method for processing of Al-containing industrial waste – Medet's sterile (IWP). The aim consists in the application of preliminary mechanical activation and next leaching by sulphuric acid thus realising a complex extraction of all useful components.

EXPERIMENTAL

An industrial waste product (*IWP*). The industrial waste product used was obtained from the Company "Medet" ore deposit in Bulgaria. Its mineral composition was: K,Na-feldspar; orthoclase – $K(AlSi_3O_8)$; plagioclase – $(Na_2O.Al_2O_3.6SiO_2)$. $2(CaO.Al_2O_3.SiO_2)$; quartz-SiO_2 and biotite $(K_2O.6Fe_2O_3.Al_2O_3.6SiO_2.\ 2H_2O)$. The chemical composition is presented in Table 1.

Table 1. Chemical composition of Al-containing industrial waste

Compound	Content (% w/w)	Compound	Content (% w/w)
Al_2O_3	9.70	SiO_2	78.11
K_2O	2.17	CuO	0.084
Na_2O	1.08	MnO	0.039
CaO	1.31	ZnO	0.042
MgO	1.65	NiO	0.005
Fe_2O_3	4.11		

Mechanical activation. The mechanical activation was performed in planetary mill "Pulverisitte 5" type. Metal balls with diameter size 20 mm were used and the intensity applied was 290 rpm. The weight ratio material:milling bodies was 1:20. The duration of activation was from 2 to 8 h.

The investigations were carried out using the method of design experiment by D-optimum plan for second order model[15] providing of the most accurate evaluation of the model coefficient $[b = (b_0, b_i, b_{ij}, b_{ii})]$. The plan was generated trough FDOP[16] on computer as an exact D-optimal plan with 15 points especially for the task. The acid decomposition with sulphuric acid, 50% w/w was performed and the quantity was calculated on the basis of the IWP composition according to the main oxides content (Al_2O_3, K_2O, Na_2O, MgO, CaO, Fe_2O_3 and FeO). Surplus of acid was used to ensure a 10:1 ratio of liquid to solid phase. The experiments were carried out in a reactor with a stirrer at constant rounds (300 rpm) in a thermostat at constant temperature. After passing of the necessary reaction time, the suspension thus obtained was filtered under vacuum and the received deposition was washed with determined constant water quantity. The filtrate together with the washing water was transferred in a 250 ml flask and after dilution was analysed for the content of Al, K, Na, Ca, Mg, Cu, Zn, Mn and Si. The content of Al (Ref. 16) and of Si (Ref. 17) was determined spectrophotometrically; Ca, Mg, Cu, Zn and Mn by atomic absorption spectrophotometry (AAS) of type "Perkin Elmer", and the determination of K and Na was done by flame photometry. On the basis of the results thus received the extent of extraction (α,% w/w) were calculated for every of the studied elements contained in IWP.

RESULTS AND DISCUSSION

The main factors influencing the decomposition process of IWP after their preliminary mechanical activation are: time of mechanical activation, intensity of milling, size of the milling bodies, ratio of material to milling bodies, temperature for acid decomposition, time for decomposition, acid concentration and ratio of liquid to solid phase. Based on the preliminary investigations three factors were chosen (x_i): time of mechanical activation (x_1); temperature for acid decomposition (x_2); and time for acid decomposition (x_3). The rest parameters keep constant values. The main factor levels and steps of the independent variables are presented in Table 2.

Table 2. Independent variables and steps

Levels	Factors		
	x_1 (min)	x_2 (°C)	x_3 (min)
Base level	360	90	75
Step	240	10	45
Low level	120	80	30
High level	600	100	120

The studied objective functions (y_i) are the extent of extraction (α, % w/w): y_1 – K, y_2 – Al, y_3 – Na, y_4 – Mg, y_5 – Ca, y_6 – Cu, y_7 – Zn, y_8 – Mn, y_9 – Si, respectively. In Table 3 the coded plan matrices and the experimental results for the objective functions are presented. The obtained extent of Al extraction was up to 88%. High is the extent of acid extraction of alkalines also (K and Na). For the case of Na it has a maximum value 100% and for K – 88%. Complete extraction (100%) was obtained for Mn but lower for Cu (61%) and for Zn. The maximum value α_{Zn} was 37%. The lowest extraction was established in the case of Ca and Si. On the basis of the design of experiments and the obtained results, the adequate regression equations (1) third order polynomials were deduced:

$$y = b_0 + \Sigma b_i x_i + \Sigma b_{ij} x_i x_j + \Sigma b_{ii} x_i^2 + \Sigma b_{iii} x_i^3 \tag{1}$$

The regression models (2-10) for the objective parameters (y_1-y_9) are as following:

$$y_1 = 80.5606 - 7.5905x_1 - 6.5749x_2 - 11.2894x_3 + 1.7294x_1x_2 - 3.1122x_1x_3 - 1.4610x_2x_3 \\ - 1.4241x_1^2 - 4.5899x_2^2 + 2.8576x_3^2 - 20.6619x_1^3 + 8.3619x_2^3 + 11.8214x_3^3 \tag{2}$$

$$y_2 = 83.3919 - 1.7615x_1 + 1.7302x_2 + 1.4691x_3 - 0.4630x_1x_2 + 0.2435x_1x_3 + 0.2160x_2x_3 \\ - 1.7323x_1^2 - 1.9634x_2^2 + 1.2698x_3^2 + 6.2276x_1^3 - 0.5531x_2^3 - 1.6706x_3^3 \tag{3}$$

$$y_3 = 80.4431 - 16.2061x_1 + 3.1931x_2 + 10.2414x_3 + 0.4187x_1x_2 - 0.8253x_1x_3 \\ - 0.4899x_2x_3 - 14.4846x_1^2 - 5.1549x_2^2 + 7.8694x_3^3 + 11.2517x_1^3 - 1.9983x_2^3 - 8.2766x_3^3 \tag{4}$$

Table 3. Plan of the matrice and values of the objective functions (α % w/w)

Factors			Objective parameters								
x_1	x_2	x_3	y_1	y_2	y_3	y_4	y_5	y_6	y_7	y_8	y_9
− 1	− 1	− 1	72.92	75.33	35.16	25.88	0.174	54.10	16.43	41.67	0.072
− 1	0	0	74.65	78.50	37.66	25.38	0.174	54.66	15.71	77.17	0.029
1	1	− 1	85.06	86.46	93.75	26.26	0.240	40.86	32.50	100.00	0.020
0	0	− 1	81.60	85.65	89.84	26.50	0.214	57.65	14.28	96.25	0.010
1	1	1	81.60	87.37	100.00	27.64	0.294	59.33	45.00	100.00	0.007
− 1	1	1	79.86	77.98	42.97	26.51	0.214	58.02	16.78	77.50	0.010
− 1	− 1	1	76.38	74.14	46.88	27.01	0.214	55.22	18.83	77.92	0.031
0	1	0	78.12	82.38	78.13	26.26	0.200	54.48	18.93	98.33	0.024
1	− 1	0	72.90	84.58	85.94	27.14	0.214	56.72	15.00	100.00	0.023
− 1	1	− 1	69.44	78.27	41.56	26.63	0.187	55.41	15.36	75.83	0.016
1	0.5	0.5	76.38	86.37	100.00	27.38	0.214	58.02	14.28	100.00	0.020
− 0.5	− 0.5	0.5	85.06	82.56	70.30	26.38	0.200	57.65	16.07	79.58	0.048
− 0.5	0.5	− 0.5	86.80	83.40	62.50	27.01	0.240	58.02	26.43	84.58	0.023
0.5	− 0.5	1	76.38	82.86	89.84	25.76	0.214	54.66	16.43	100.00	0.014
1	− 0.5	− 0.5	90.27	84.00	91.25	27.39	0.187	55.04	14.65	100.00	0.017

$$\begin{aligned} y_4 = 25.9511 - 2.0141x_1 + 0.7017x_2 - 0.3307x_3 - 0.2411x_1x_2 + 0.1259x_1x_3 - 0.4549x_2x_3 \\ + 0.3052x_1^2 + 0.1749x_2^2 + 0.5478x_3^2 + 2.5874x_1^3 - 0.8512x_2^3 + 0.6600x_3^3 \end{aligned} \tag{5}$$

$$\begin{aligned} y_5 = 0.1885 - 0.06897x_1 + 0.03054x_2 - 0.02652x_2 + 0.00422x_3 + 0.00646x_1x_2 \\ - 0.00478x_2x_3 - 0.00876x_1^2 + 0.00801x_2^2 + 0.03403x_3^2 + 0.09244x_1^3 \\ - 0.02199x_2^3 + 0.04696x_3^3 \end{aligned} \tag{6}$$

$$\begin{aligned} y_6 = 56.4456 - 9.0785x_1 + 2.7885x_2 + 2.5316x_3 - 2.6343x_1x_2 + 2.4850x_2x_3 \\ + 1.8906x_1x_3 - 1.3918x_1^2 - 1.6731x_2^2 + 1.7418x_3^2 + 8.8296x_1^3 - 4.2838x_2^3 + 0.5313x_3^3 \end{aligned} \tag{7}$$

$$\begin{aligned} y_7 = 12.6520 - 16.7291x_1 - 0.1157x_2 - 15.1405x_3 + 5.7247x_1x_2 + 2.8777x_2x_3 \\ - 0.6776x_1x_3 + 1.4803x_2x_3 + 3.7285x_1^2 + 3.7285x_2^2 + 4.0544x_3^2 + 20.2163x_1^3 \\ + 5.0041x_2^3 + 19.0701x_3^3 \end{aligned} \tag{8}$$

$$\begin{aligned} y_8 = 15.5271 + 25.6295x_1 + 4.1161x_2 - 3.5014x_3 + 0.8051x_1x_2 - 0.4048x_2x_3 \\ + 0.2330x_1x_3 - 8.7682x_1^2 + 2.3578x_2^2 - 1.0801x_3^2 - 13.6867x_1^3 - 4.4060x_2^3 + 2.8152x_3^3 \end{aligned} \tag{9}$$

$$\begin{aligned} y_9 = 0.02475 - 0.01948x_1 - 0.02326x_2 + 0.01010x_3 + 0.00987x_1x_2 + 0.00334x_2x_3 \\ + 0.00414x_1x_3 + 0.00035x_1^2 + 0.01019x_2^2 - 0.01259x_3^2 + 0.01067x_1^3 \\ + 0.01359x_2^3 - 0.01734x_3^3 \end{aligned} \tag{10}$$

Using the developed regression model for every objective parameter, an optimisation was done searching of a compromise decision of the parameters from y_1 to y_9 (Ref. 18) at maximum for y_1 to y_8 and minimum for y_9 required. A grid search method has been used for finding the optimum conditions. As the method ensures a finding of global optimum, 20 variations of compromise optimal regimes ordered according to the values of the function of losses were printed (minimal difference for every y_i of reference value).

$$\phi = \Sigma\,(y_{i\,\mathrm{calc}} - y_{i\,\mathrm{ref}})^2 \,/\, \Sigma\,(y_{i\,\mathrm{max}} - y_{i\,\mathrm{min}})^2 \tag{11}$$

where $y_{i\ \mathrm{calc}}$ is calculated value; $y_{i\ \mathrm{ref}}$ – reference value; $y_{i\ \mathrm{max}}$ – maximum value; $y_{\mathrm{i\ min.}}$ – minimum value.

Using the developed regression models two-dimensional diagrams representing the influence of two factors on the parameter y are drawn up (Figs 1-6). As a result the following optimum conditions were established: time for mechanical activation (x_1) = 576 min, temperature for acid treatment (x_2) = 92°C, time for acid decomposition (x_3)=120 min. At these conditions values obtained were: α_{Al}=88%; α_{K}=87%; α_{Na}=100%; α_{Mn}=100%; α_{Cu}=61% and α_{Zn}=37%. Si was not affected during the acid treatment at all. The composition of the obtained acid extract presented in mg cm^{-3} is: $Al_2(SO_4)$ – 2300; K_2SO_4 – 280; Na_2SO_4 – 200; $CuSO_4$ – 8.2; $ZnSO_4$ – 2.4 and $MnSO_4$ – 6.6. After evaporation of this extract alums could be obtained and after their reductive decomposition Al_2O_3 and alkaline salts would be obtained.

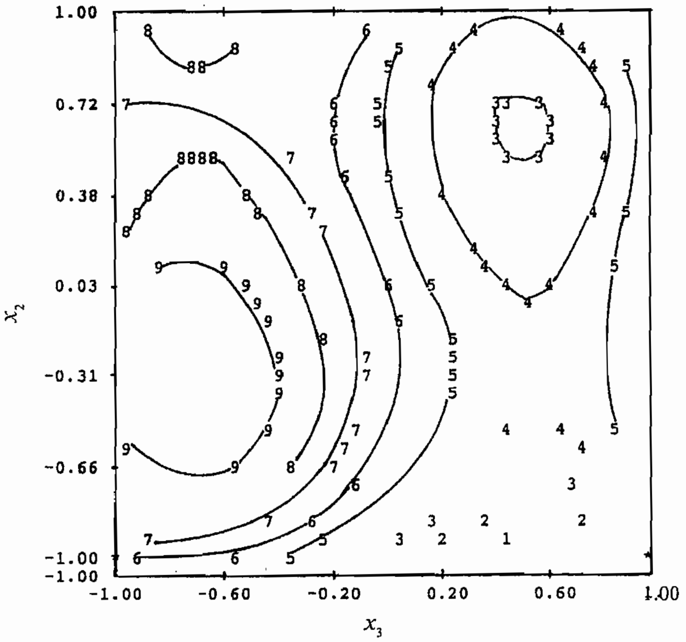

Fig. 1. Two-dimensional diagram for the influence of x_2 and x_3 on the parameter y_1 at optimum value of $x_1 = 0.90$. Value of y_1 for different levels: 1 – 67.1614; 2 – 69.3704; 3 – 71.5793; 4 – 73.7882; 5 – 75.9972; 6 – 78.2061; 7 – 80.4150; 8 – 82.6240; 9 – 84.8329

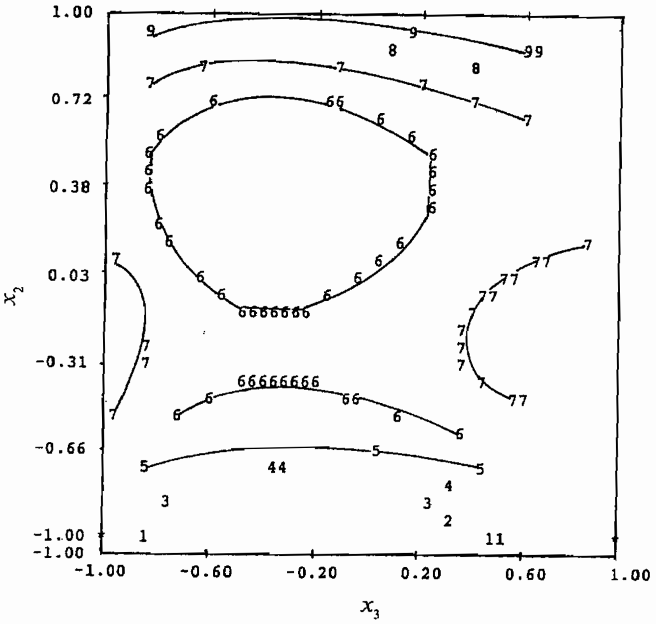

Fig. 2. Two-dimensional diagram for the influence of x_1 and x_3 on the parameter y_2 at optimum value of $x_2 = 0.30$. Value of y_2 for different levels: 1 – 78.6610; 2 – 79.6901; 3 – 80.7193; 4 – 81.7484; 5 – 82.7748; 6 – 83.8068; 7 – 84.8359; 8 – 85.8651; 9 – 86.8943

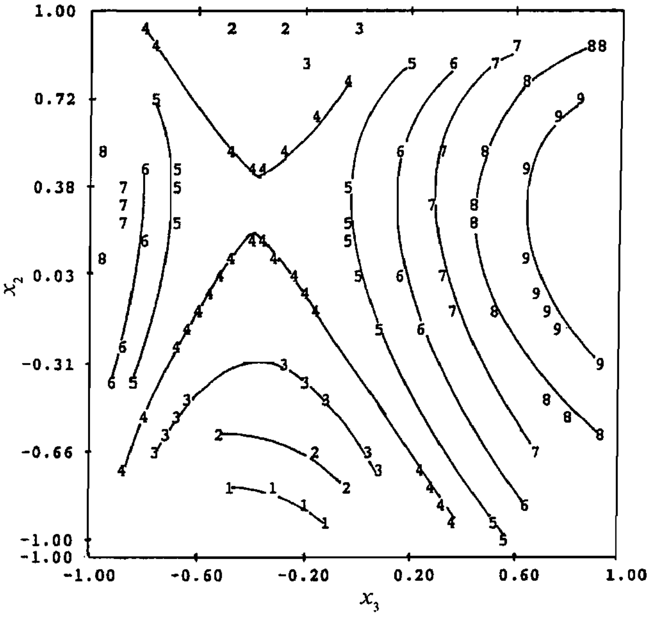

Fig. 3. Two-dimensional diagram for the influence of x_2 and x_3 on the parameter y_3 at optimum value of x_1 = 0.90. Value of y_3 for different levels: 1 – 84.4094; 2 – 86.2534; 3 – 88.0975; 4 – 89.9415; 5 – 91.7856; 6 – 93.6296; 7 – 95.4737; 8 – 97.3177; 9 – 99.1617

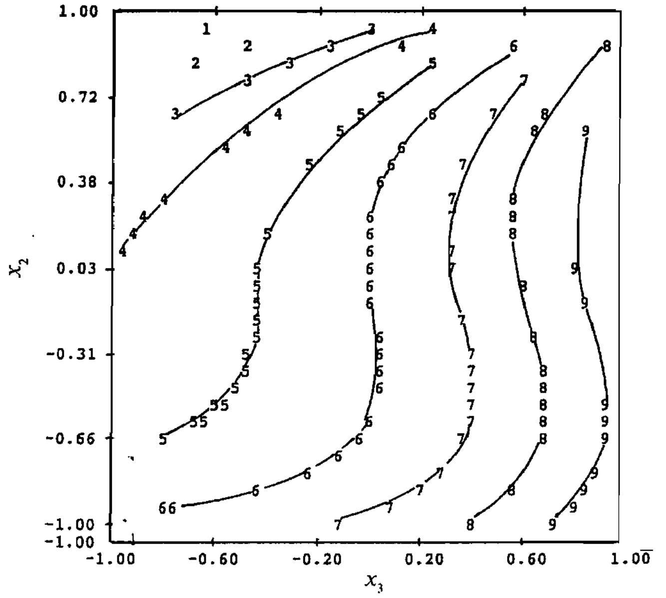

Fig. 4. Two-dimensional diagram for the influence of x_2 and x_3 on the parameter y_4 at optimum value of x_1 = 0.90. Value of y_4 for different levels: 1 – 44.4425; 2 – 46.2881; 3 – 48.1336; 4 – 49.9792; 5 – 51.8248; 6 – 53.6704; 7 – 55.5160; 8 – 57.3616; 9 – 59.2071

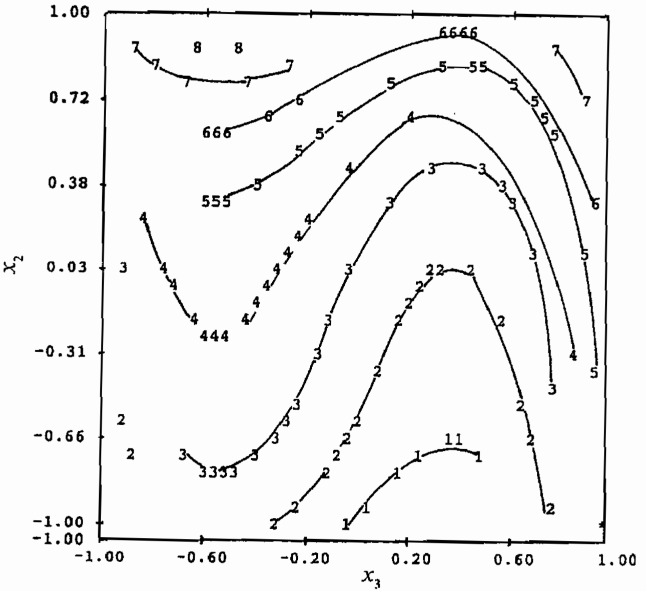

Fig. 5. Two-dimensional diagram for the influence of x_2 and x_3 on the parameter y_5 at optimum value of $x_1 = 0.90$. Value of y_5 for different levels: 1 – 7.3897; 2 – 10.7018; 3 – 14.0138; 4 – 17.3258; 5 – 20.6379; 6 – 23.9499; 7 – 27.2619; 8 – 30.5740; 9 – 33.8860

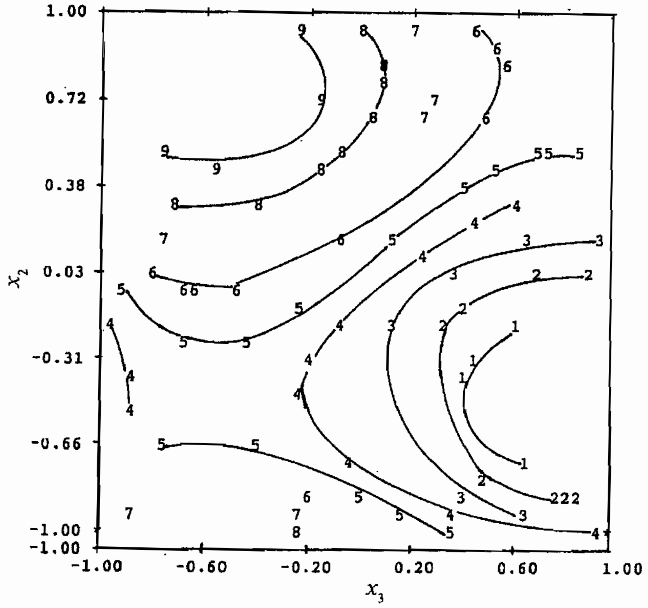

Fig. 6. Two-dimensional diagram for the influence of x_2 and x_3 on the parameter y_6 at optimum value of $x_1 = 0.90$. Value of y_6 for different levels: 1 – 95.5936; 2 – 96.4018; 3 – 97.0995; 4 – 98.0181; 5 – 98.8263; 6 – 99.0344; 7 – 99.4426; 8 – 99.8082; 9 – 99.9899

CONCLUSIONS

These investigations demonstrate the possibility to combine preliminary mechanical activation and acid extraction using sulphuric acid for "Medet's sterile" (IWP) waste that according to its mineral content could be numbered among nonbauxite Al-containing raw materials. Using the method of the design experiment the influence of the main parameters: time for mechanical activation, temperature and time for acid extraction with sulphuric acid on the extraction extent of the useful components from IWPMA was studied. Basing on the deduced regression models the optimisation of the process was done and the optimum conditions for highest extraction of Al, K, Na, Cu and Mn were determined. The proposed method offers a possibility for complex processing of "Medet's sterile".

REFERENCES

1. K . UMLAUT: Hutnic, **32**, 272 (1982).
2. B. KOUMANOVA, M. DRAME, M. POPANGELOVA: Resources, Conservation and Recycling, **19**, 11 (1997).
3. B. KOUMANOVA, M. DRAME, M. POPANGELOVA: Compt. rend. de l'Acad. Bulg. des Sci., **48**, 8 (1995) (in Bulgarian).
4. Author's Certificate USSR , 1971, No 211526.
5. Author's Certificate USSR , 1973, No 389 019.
6. Author's Certificate USSR , 1976, No 484185.
7. Pat. France, 1975, No 7 430 396.
8. M. MANVELJAN: Review of the Erevan NIICh, Erevan, 1964.
9. Author's Certificate Bulgaria, 1974, No 27 942.
10. T. M. KUSZNEZOVA, L. M. SULIMENKO: TIZ Fachberichte, **109**, 424 (1985).
11. H. J. HUHN, H. HEEGN, G. LUDWIG, C. BERHARDT: Silikattechnik, **29**, 376 (1978).
12. E.S. LAPTEVA, T. S. USUPOV, A. S. BERGER: Physico-chemical Changes of Layer Silicates in the Process of Mechanical Activation. Nauka, Novosibirsk, 1981.
13. A. TONEVA, I. DOMBALOV: J. of the Balkan Tribol. Assoc., (1-2), 149 (1994) (in Bulgarian).
14. I. DOMBALOV, A. TONEVA, I. GRUNCHAROV, J. PELOVSKI: Thermochimica Acta, **148**, 479 (1989).
15. N. ELENKOVA, R. ZONEVA, Z. NEDELCHEVA, D. BOIKOVA, R. VESELINOVA, TONKOVA: Metallurgia, **4**, 28 (1980) (in Bulgarian).
16. N. ELENKOVA, R. TZONEVA, Z. NEDELCHEVA, D. BOIKOVA, R. VESELINOVA, N. TONKOVA: Metallurgia, (4), 28 (1980) (in Bulgarian).
17. R. AILER: Chemistry of Silicon. Mir, Moscow, 1982.
18. H. A. YONCHEV: Intern. Conf.-Workshop, Neuchatel (Eds Y. Dodge, V. V. Fedorov, H. P. Wyun). Elsesier Science Publishers B.V., 1988.

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