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Zinc Sulfide Concentrates and Optimization of their Roasting in Fluidezed Bed Reactor

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***Abstract*—The production of glass, ceramic materials and many non-ferrous metals (Zn, Cu, Pb, etc.), ferrous metals (pig iron) and others is connected with the use of a considerable number of initial solid raw materials. Before carrying out the basic technological processes (oxidized roasting, melting, agglomeration, baking) it is necessary to mix and homogenize the raw materials that have different chemical and phase content, granulometry and humidity. For this purpose zinc sulfide concentrates differing in origin are studied for their more complete characteristics using chemical, X-ray diffraction analyses, DTA and TGA as well as Mössbauer spectroscopy. The phases established in most concentrates are: β-ZnS, mZnS.nFeS, FeS_2, $CuFeS_2$, PbS, SiO_2 (α-quartz).

With the help of the developed by us a Web-based information system for a continued period of time different mix proportions from zinc concentrates are calculated and used in practice (roasting in fluidized bed reactor), which have to conform to the technological requirements of the zinc hydrometallurgical technological scheme.

***Keywords*—fluidized bed reactor, roasting, Web-based information system, zinc concentrates.

I. Introduction

VERY often in zinc production by the hydrometallurgical method 6-10 initial zinc concentrates (of different origin) are used [1-3], as well as some semi-finished products. In most plants the content of 18 components and the humidity of the concentrates and the mix obtained from them are monitored. Some of them (Zn, S) are controlled by setting their minimum value necessary for the stable operation of the fluid bed reactor [4-10] and maintaining the necessary temperature (900-950 ^oC). For the other components contained in the zinc concentrates (Fe, SiO_2, Ga, In, Tl, Ge, As, Sb, etc.) a maximum content is determined, which depends on the used technological scheme [11]. A large part of the technological processes are directed toward obtaining a $ZnSO_4$ solution with a strictly determined content of impurities, which would allow for high purity cathode zinc (SHG) to be obtained by electrolysis at the best technical-economic indexes. In this regard the selection of a suitable proportion for the sulfide zinc concentrates and their homogenization before and during roasting are decisive.

In this connection, the goal of this study is to characterize by different methods zinc concentrates processed in Bulgaria and with the expert Web-based information system to calculate the optimal mixing proportions for roasting in fluidized bed furnaces from the studied concentrates.

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II. Results and discussion

The work of the fluidized bed furnace (FBF) (Fig 1) as a basic energy and technological link in the process of hydrometallurgical zinc production significantly influences the indexes of the process of production. The indexes of roasting depend on the technological regime, the FBF construction and to a great degree on the characteristics of the processed raw materials [12-20].

In order to be able to control roasting in FBF a more complete information is necessary about the influence of the concentrates and the products from their oxidation roasting on the indexes of the roasting process. The place of the oxidation roasting process in FBF in the technological scheme for zinc production is presented in Fig 2. It shows where the developed Web-based information system for zinc mix calculation is used. It is crucial for the optimal implementation of the oxidation process in FBF, the obtaining of a suitable in its content zinc calcine and all following processes – leaching, purification, electrolysis.

The chemical composition of the studied concentrates is shown in table I. The origin of the studied concentrates is from: 1- Bulgaria; 2 – Peru; 3, 4- Serbia; 5, 6 – Macedonia; 7 – Bosnia&Herzegovina; 8 – Greece; 9 – Turkey.

The process of zinc calcine leaching depends heavily on its phase composition. To a great degree it is determined by the initial phase and chemical composition of the concentrates, the roasting regime and the work of FBF. In this connection, a study of zinc concentrates in relation to their phase composition was performed by X-ray diffraction analysis. The obtained general results are presented in table II.

The place of the developed software in the discussed scheme is in the process selection of raw materials and their suitable mixing. The goals in this specific case are:

- Obtaining of a zinc calcine with a suitable chemical content
- To have the processes of ferrite formation and silicate formation take place at the lowest possible degree
- Content of Zn and S in the calcine not less than 50 % for Zn and 31 % for S
- Limiting the content of Pb, Fe, SiO_2, Ge, Sb, As, Cl, CaO, F below the maximum admissible values. These values can be adjusted when necessary or when the technological scheme for calcine processing is changed.

In all concentrates a basic phase is β-ZnS. The possible inclusion of a part of ZnS as marmatite ($Zn_xFe_{1-x}S$) was determined on the basis of the obtained Mössbauer spectra according to the distribution of iron between the phases ZnS, FeS_2 and $CuFeS_2$.

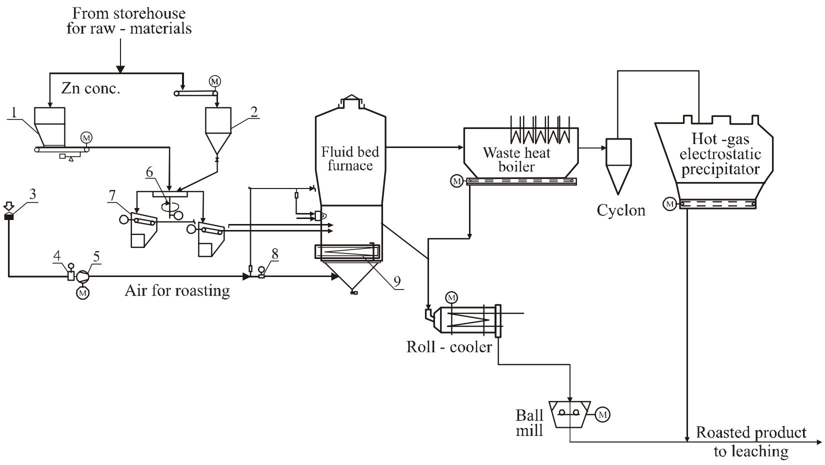

Fig. 1 Technological scheme of roasting in fluid bed: 1 - hopper for Zn concentrate; 2 - hopper for start calcine; 3 - protective filter; 4 - air–cushion; 5 - air-compressor; 6 - disk feeder; 7 - slinger conveyor; 8 - motor valve; 9 - cooling elements

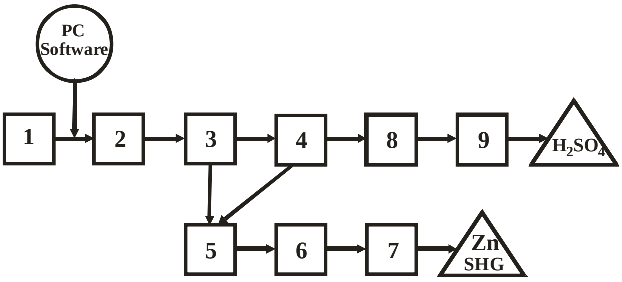

Fig. 2. Block-scheme of zinc production: 1 – storehouse for raw-materials; 2 - mixing; 3 – roasting in FBF; 4 – gas cleaning; 5 – zinc calcine leaching; 6 – purification of $ZnSO_4$ solution; 7 – electroextraction; 8 – SO_2 oxidation; 9 – SO_3 absorption

The application of modern software for calculation and prognosis of the chemical and phase composition of the mix proportions of concentrates can lead to a significant improvement of the technical and economic indexes of the technological processes. This can have a great economic efficacy with the processing of non-standard raw materials along with concentrates conforming to basic requirements.

The Web-based information system is built on a modular principle using server programming language PHP. Its main modules provide opportunities for construction, management and use of Web-based database of zinc concentrates [3, 20] in the management control system relational database MySQL [21-24]. Particular attention is paid to the creation of interactive convenient mechanisms for consumers of type Customer and Student generating a main database of all the concrete work concentrates on the search and calculation of the stock on predefined and stored restrictive conditions for different components of stock. In realization of the process of searching for recipes stock required the use of recursive algorithms because of various possibilities for combining concentrates on five different levels - one optimized level and four additional levels, which are allocated work concentrates selected.

Issue expert system allows three types of users to operate it via the Internet (Fig 3 and Fig 4). The main difference between the client (commercial users) and the student is to major operations over a database containing information on all arable concentrates from different providers (different prices) and from different countries, in principle such data are private information. Students are given an operating test basic database, which is available from the literature. From the main database for both types of users in their choice of work is generated database containing some of the concentrates (available now). It was undergoing treatment being selected mode. In automatic mode, look for all combinations of concentrates that meet the restrictive conditions put in place for their lower and upper limits and the step change. Intentions stock is calculated and displayed different values, important for the production of zinc, it is possible that the stock of sorting selected criterion. There is a possible change to the restrictive conditions of steps to amend the boundaries of the selected new step and repeat the automatic mode. In a specific mode is selected data set concentrates and immediately calculates and displays a stock.

The expected results from implementation of Web-based information system expertise as implemented activities and processes could be summarized as follows:

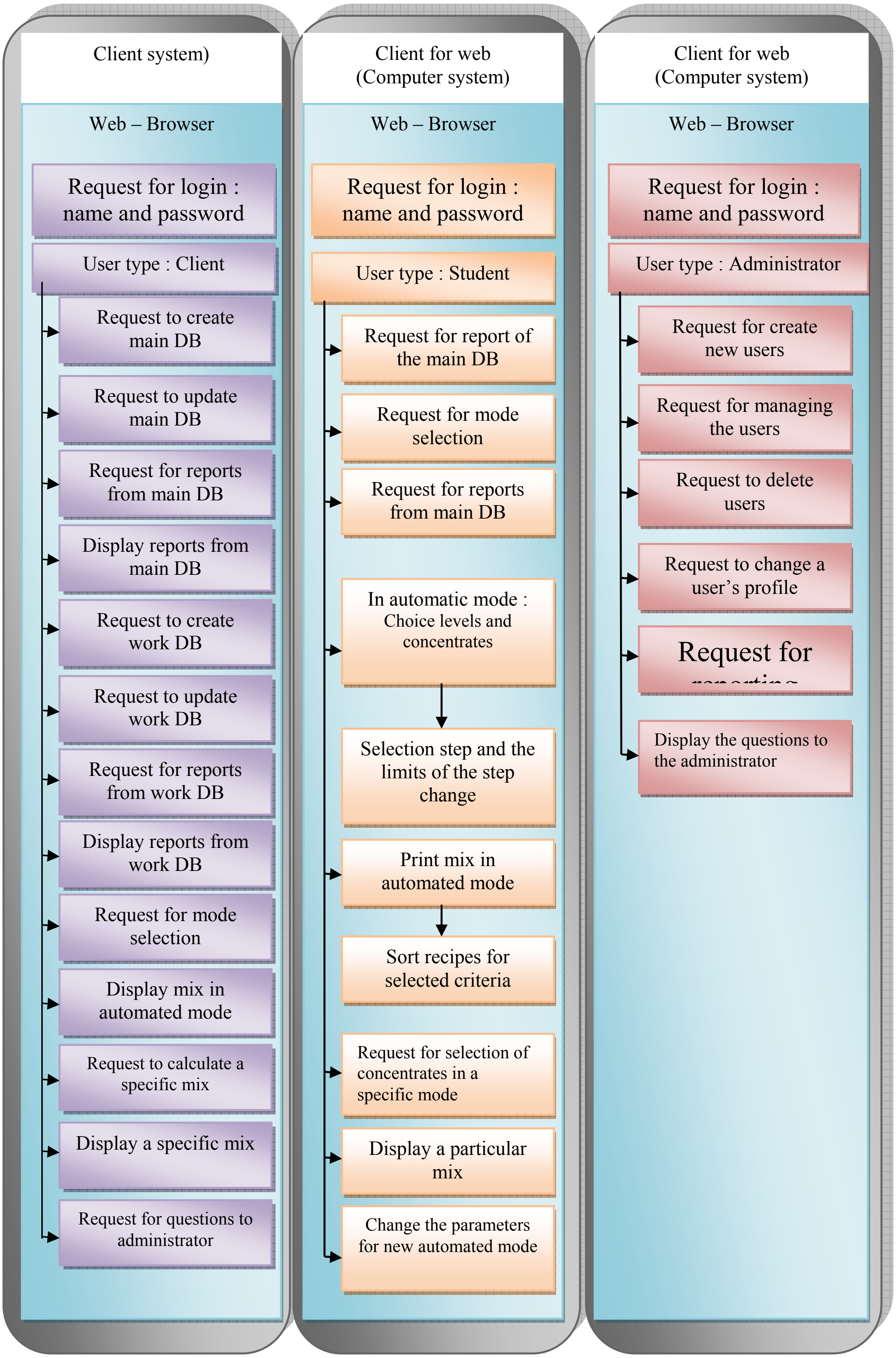

Fig. 3 Computer system for the clients with applications

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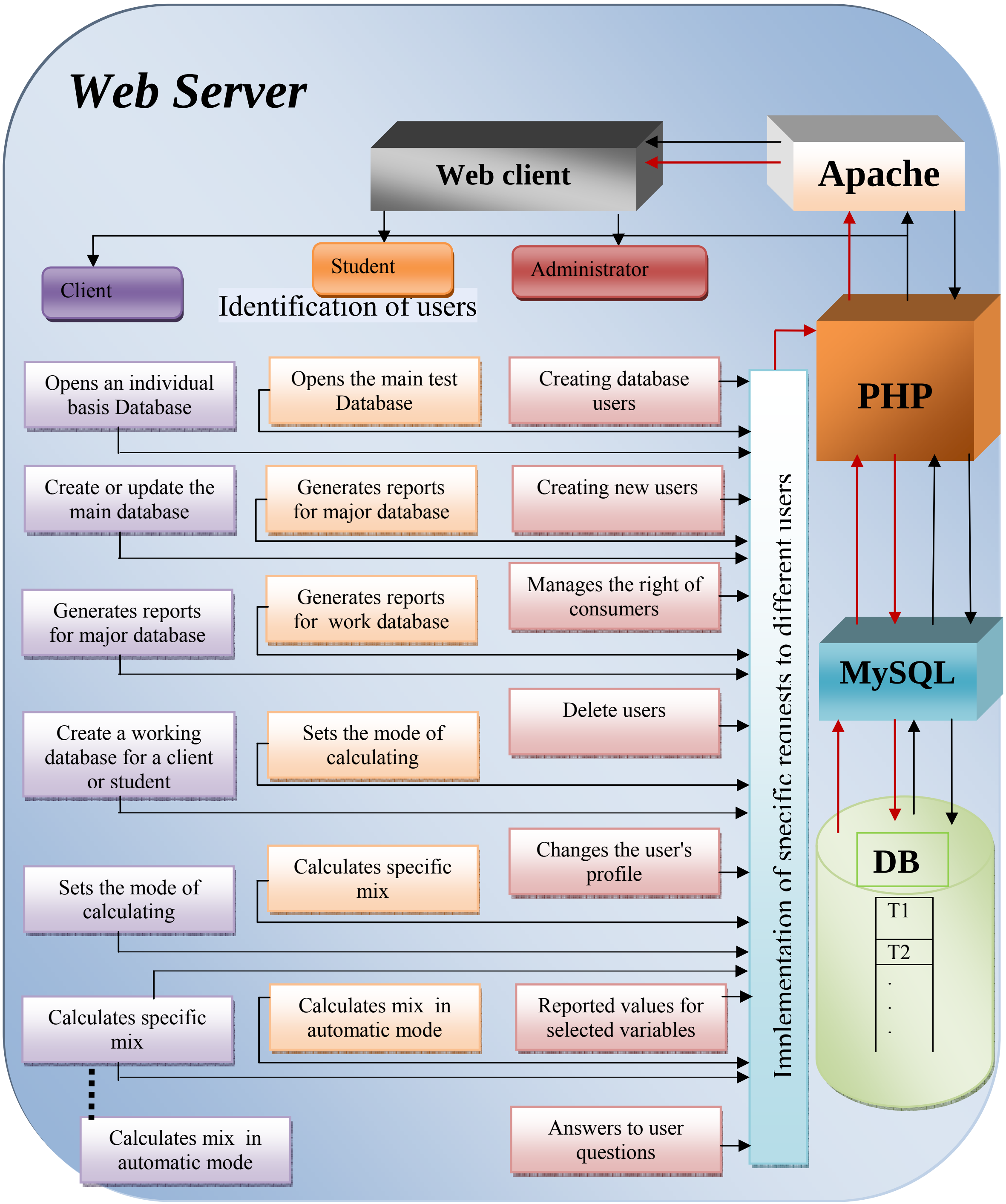

Fig. 4 Scheme of the Web server and applications

TABLE I
CHEMICAL COMPOSITION OF THE STUDIED ZINC CONCENTRATES

Component	Concentrate, (%)								
	1	2	3	4	5	6	7	8	9
Zn	49.3	53.75	47.16	49.8	50.22	55.25	48.72	50.37	46.45
S_{total}	30.0	32.20	32.85	31.75	32.3	31.35	33.5	33.5	32.50
Cu	1.96	0.55	1.52	0.22	0.53	0.98	0.3	0.21	2.06
Cd	0.29	0.09	0.36	0.28	0.26	0.42	0.49	0.3	0.23
Co	0.006	0.002	0.01	0.001	0.001	0.01	0.001	0.001	0.056
Ni	0.002	0.001	0.006	0.001	0.001	0.001	0.001	0.002	0.003
Al_20_3	0.17	0.14	0.35	0.17	0.5	0.28	0.08	0.05	0.38
Tl(g/t)	-	5	11	7	15	9	10	11	8
Pb	2.85	0.56	0.85	1.75	2.77	3.31	1.89	1.06	2.65
Fe	6.9	9.05	13.15	11.46	6.8	4.69	13.22	10.85	9.75
SiO_2	2.25	1.70	2.2	1.85	4.55	1.9	0.62	0.95	3.30
Ge(g/t)	5	5	5	5	5	5	5	5	5
Sb	0.001	0.001	0.001	0.064	0.027	0.001	0.012	0.02	0.002
As	0.002	0.02	0.007	0.04	0.13	0.002	0.18	1.02	0.05
MgO	0.08	0.13	0.09	0.08	0.06	0.13	0.1	0.07	0.07
CaO	0.38	0.14	0.45	0.09	0.12	0.38	0.4	0.3	0.43
Cl	0.01	0.011	0.01	0.012	0.009	0.01	0.011	0.01	0.01
F	0.008	0.013		0.01	0.01	0.01	0.008	0.005	0.01

TABLE II (A)
RESULTS FROM THE X-RAY DIFFRACTION ANALYSIS OF ZINC CONCENTRATES

	Concentrates / phases			
N	1	2	3	4
1	β-ZnS ($Zn_{0.94}Fe_{0.06}S$)	β-ZnS ($Zn_{0.86}Fe_{0.14}S$)	β-ZnS ($Zn_{0.80}Fe_{0.20}S$)	β-ZnS ($Zn_{0.85}Fe_{0.15}S$)
2	FeS_2		FeS_2	FeS_2
3	$CuFeS_2$	$CuFeS_2$	$CuFeS_2$	$CuFeS_2$
4	SiO_2			SiO_2
5	PbS	PbS	PbS	PbS

TABLE II (B)
RESULTS FROM THE X-RAY DIFFRACTION ANALYSIS OF ZINC CONCENTRATES

N	Concentrates / phases				
	5	6	7	8	9
1	β-ZnS ($Zn_{0.98}Fe_{0.02}S$)	β-ZnS ($Zn_{0.96}Fe_{0.04}S$)	β-ZnS ($Zn_{0.86}Fe_{0.14}S$)	β-ZnS ($Zn_{0.9}Fe_{0.1}S$)	β-ZnS ($Zn_{0.88}Fe_{0.12}S$)
2	FeS_2	FeS_2	FeS_2	FeS_2	FeS_2
3	$CuFeS_2$	$CuFeS_2$	$CuFeS_2$	$CuFeS_2$	$CuFeS_2$
4	SiO_2				SiO_2
5	PbS	PbS	PbS	PbS	PbS

1. Accelerating the process of determining the mix of zinc concentrates using modern software technology client-server Internet programming (HTML, DHTML, XML, JavaScript, CSS, Web-server Apache, server programming language PHP, management system for relational MySQL databases, etc.)
2. Facilitate the operation of data concentrates and special attention is paid to update their operations - adding, changing and deleting as the main and working concentrates. Comfortable selecting and importing work concentrates on the main database - up to 15 working concentrates, as at any time to control the number and concentrates itself on user-selected levels.
3. Determination of all possible mix in automatic mode in interactive mode selected in restrictive conditions, lower limit, upper limit and step of change for working concentrates down five levels as well as establishment of optimal mix of user selected criteria.
4. Change the restrictive conditions of the user and repeat the process for automated calculation of all possible mix under the new restrictive conditions and calculation of mix by a specific set of values for chemical technology selected by their concentrations, without verifying restrictive conditions.
5. Show all important production parameters such as zinc concentrate mixes chemical composition, chemical composition of calcine, phase composition of the calcine and others.
6. Easier administration of different users according to their profile, which is related to their access rights to the underlying database.
7. Providing software tools for multiplying the impact of the system for production of lead, copper, glass and others.

In the calculation of mix proportions from the zinc concentrates from Table 1 in automatic regime it was worked with a different step of change of the different concentrates (6 tons, 7 tons, 10 tons, 5 tons or % correspondingly) A part of the general data for this calculation at a step of 5 tons (%) is given in table III.

It is clear from the data that in the period it was worked with 9 zinc-containing raw materials and conditions are established for the finding of recommended mix recipes. The maximum solubility of Zn in 7 % solution of H_2SO_4 for the best recipes varies in the range of 91,27- 92,95 %. The best proportions (A – H) using 7, 8 or 9 zinc concentrates are presented in Table IV.

III. CONCLUSIONS

1. Sulfide concentrates differing in origin are studied for their more complete characteristics. For this purpose chemical and X-ray diffraction analyses as well as DTA and TGA were used. The phases established in most concentrates are: β-ZnS, mZnS.nFeS, FeS_2, $CuFeS_2$, PbS, SiO_2 (α-quartz).

2. With the help of X-ray phase analysis and Mössbauer spectroscopy it was established that in the zinc concentrates the values of x in the narmatite formula ($Zn_xFe_{1-x}S$) are observed.

3. With the help of the developed Web-based information system for a continued period of time different mix proportions from zinc concentrates are calculated, which have to conform to the technological requirements of the zinc hydrometallurgical technological scheme. As an optimizing criterion zinc maximum soluble in a 7% solution of sulfuric acid was used.

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TABLE III
DATA FROM CALCULATION OF MIX PROPORTIONS IN AUTOMATIC REGIME

Mix calculation, N	Number of concentrates	Step, %	Recommended mix recipes	Max. Zn (soluble in H_2SO_4), %
1	7	3	95	92.95/A
2	8	3	88	92.68/B
3	9	3	77	92.42/C
4	7	5	15	92.19/D
5	8	5	10	91.73/E
6	9	5	6	91.27/F
7	7	7	10	92.13/G
8	8	7	6	91.52/H
9	9	7	0	-

TABLE IV
BEST PROPORTIONS OF ZINC CONCENTRATES

Proportion	Concentrate N/%								
	1	2	3	4	5	6	7	8	9
A	6	19	-	3	6	57	-	3	6
B	6	19	3	3	6	54	-	3	6
C	6	19	3	3	6	51	3	3	6
D	10	20	-	5	10	40	-	5	10
E	10	20	5	5	10	35	-	5	10
F	10	20	5	5	10	30	5	5	10
G	7	23	-	7	7	42	-	7	7
H	7	23	7	7	7	35	-	7	7