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OPTIMIZATION OF OXIDIZED ZINC-CONTAINING ORES PROCESSING TECHNOLOGY

The article contains the results of the studies regarding the composition of oxidized zinc-containing raw materials on the example of "Shaimerden" deposit ore, Kostanai region, the Republic of Kazakhstan. It also shows the relevance of this raw material use for the national economy and the need to optimize the existing technological scheme for more complete extraction of valuable components, as well as the analysis of the technical and economic assessment of this type of raw material processing.

Keywords: *oxidized zinc-containing ore; ore deposit; ore processing.*

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ОПТИМІЗАЦІЯ ТЕХНОЛОГІЇ ПЕРЕРОБКИ ОКИСЛЕНИХ ЦИНКОМІСТКИХ РУД

У статті наведено результати досліджень речовинного складу окисленої цинкомісткої сировини на прикладі руди з родовища «Шаймерден» Костанайської області (Республіка Казахстан). Доведено актуальність використання даного різновиду сировини для національного господарства, а також необхідність оптимізації діючої технологічної схеми з метою найповнішого отримання цінних компонентів з руди. Також проведено техніко-економічне оцінювання переробки даного виду сировини.

Ключові слова: *окислена цинкомістка руда; рудне родовище; переробка руди.*
Рис. 4. Табл. 7. Літ. 11.

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ОПТИМИЗАЦИЯ ТЕХНОЛОГИИ ПЕРЕРАБОТКИ ОКИСЛЕННЫХ ЦИНКСОДЕРЖАЩИХ РУД

В статье приведены результаты исследований вещественного состава окисленного цинксодержащего сырья на примере руды месторождения «Шаймерден», Костанайской области (Республика Казахстан). Подтверждена актуальность использования данного вида сырья для национального хозяйства и необходимость оптимизации действующей технологической схемы с целью наиболее полного извлечения ценных компонентов. Также проведена технико-экономическая оценка переработки данного вида сырья.

Ключевые слова: *окисленная цинксодержащая руда; рудное месторождение; переработка руды.*

Problem statement. Production of mineral raw materials for the world markets, despite the decline in non-ferrous metals and gold prices, gives a significant share of exchange earnings which are necessary for further extraction and processing of mineral raw materials in Kazakhstan.

Currently, zinc consumption increases continuously because of the expansion of its application field. The average annual increase of zinc consumption is about 10% (Tarasov, 2005).

At the same time, in recent years there has been a tendency of raw material quality loss due to the reduction of stocks of crude sulphide and polymetallic and copper-zinc ores and increase in the volume of zinc-containing refractory ores processing.

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Off-balance zinc carbonates of Zhairem ore were classified as zinc oligonite type of ore with the average grade of zinc 2.53 mas% (Tyan, 1981). Zhairem carbonate ores always contain 4 cations – zinc, iron, manganese and potassium. These cations occupy dual position in carbonates structure, forming simple or complex minerals, depending on initial concentration.

Processing complexity arises because of the variability of minerals composition in oxidized ore (Tyan, 1981).

Owing to their technological properties, zinc carbonate ores of Zhairem are non-washable mineral raw materials for flotation. Flotation of zinc carbonates with preliminary hot sulphidation by sodium sulfide at the temperature of 40–60 0C and activation with the use of copper sulfate method according to Andreyeva–Davis method (Abramov, 1986) did not have positive results (Tyan, 1992).

Hydrometallurgical processing of zinc carbonate ores by agitation and heap leaching contributed to obtaining quite modest technological parameters (Tyan, 1992).

Due to low technological parameters obtained by processing of zinc carbonate ores (oxidized ores) of the Zhairem deposit, they were transferred to the category of off-balance materials (Tyan, 1981).

Oxidized zinc ore of "Shaimerden" deposit is located in North-West Kazakhstan. It is unique in zinc resources and zinc content (1.26 mln tons of reserves with zinc contents of 27.2–29 mas%) (Palenova, 2010).

The oxidized ores of "Shaimerden" deposit are presented by zinc minerals, related to carbonates and silicates. Carbonates and silicates of zinc are often found together. Willemite and franklinite hardly ever can be found together. The degree of minerals growth and waste rock is very different. Waste rock is represented by limestone, dolomite, quartz, clay and various iron oxides.

The problems in determining the mineralogical and phase analyses of oxidized zinc ore of the deposit are the result of a complex mineral composition, as well as the presence of sludge and soluble salts.

The complex mineralogical composition of oxidized zinc ores creates some problems in determining the actual chemical analysis of mineral raw materials. On the other hand, technological parameters of zinc oxide minerals enrichment are adequate to their material composition.

In this situation, it is necessary to conduct the chemical phase analysis (CPA) using the method of selective solution while studying the material composition of complex mineral raw materials (Filippova, 1975).

It becomes obvious that in the case of studying the material composition of oxidized zinc ores, it is necessary to define all forms of zinc compounds present in the ores material according to the chemical phase analysis.

Thus, an integrated approach to determining the material composition of the complex oxidized mineral raw material allows avoiding mistakes when selecting the optimum technology for processing.

Latest publications analysis. Currently, zinc-containing oxidized ore is processed by a complex technological scheme, including the following process stages as roasting to produce roasted product, Waelz process, leaching, electrolytic process and zinc cathode smelting to produce final marketable products. Theoretical and practical issues of similar raw material processing are given such works A.A. Abramov (1986), L.A. Kazanbayev (2007), E.E. Palenova (2010), N.A. Philipov (1975), V.D. Tyan (1992).

The aim of the study of the material composition of "Shaimerden" deposit oxidized ore is to define the basic properties of mineral raw material necessary for its qualitative characteristics and evaluation of opportunities for its profitable processing. The material composition of the oxidized ore is determined by its granulometric, mineralogical, physical and physicochemical characteristics.

The study of the material composition of the oxidized ore comprises the following phases:

- finding the mineralogical composition of the main valuable minerals in accordance with their size, interpenetration between themselves and with waste rock minerals;
- finding grain fineness of the ore which contains main valuable components by classes with its size construction characteristics;
- identification of the main physical, mechanical and chemical characteristics of ore.

Attention was paid to the study of the phase composition of oxidized zinc ore, its textural and structural features, content forms of valuable components and contaminants. Solubility of the ore in sulfuric acid, acid capacity of the ore and zinc extraction ratio in solution were also investigated for sulphuric-acid leaching.

All the abovementioned physical and chemical characteristics are the determining factors for the development of recommended technologies of enrichment and hydrometallurgical processing of the oxidized zinc ore.

Key research findings. The research object was the sample of the oxidized zinc ore of the Shaimerden deposit. The chemical composition of the original ore sample was determined by the use of inductively coupled plasma mass spectrometry. The results of the complete chemical analysis of the test sample of the oxidized ore are given in Table 1.

Table 1. **Chemical analysis of the ore samples,** *%, authors'*

Name of the components	Zn	Cu	Pb	Fe	SiO_2	Al_2O_3	CaO	MgO
Content	22.94	0.05	0.65	4.0	19.76	8.35	8.17	0.86

As it can be seen from Table 1, the investigated ore has rather high content of zinc and silicon dioxide; the content of aluminum, calcium, magnesium oxides as well as iron sulphide in the ore is low. Copper and lead sulphides are present in small amounts.

The microstructure of the ore samples was investigated by means of scanning electron microscope JSM6390L (production of Japanese company JEOL), equipped with the system of energy dispersive microanalysis (EDS) INCAEnergy (OXFORD Limited, UK).

Studies of ore phase composition conducted on X'Pert PRO diffractometer showed that it is predominantly in the form of carbonates and silicates, and it is less common in the form of sulphides and aluminosilicates. The research results on the spectra are shown in Table 2.

Table 2. **The results of energy dispersive microanalysis of the studied ore,** *authors'*

	Elements, %															Total
	O	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ca**	**Ti**	**Mn**	**Fe**	**Zn**	**As**	**Br**	**Pb**	
Spectrum 1	23.21		0.77	1.40	4.64		2.43	2.00			0.57	4.32	1.99		58.67	100.00
Spectrum 2	23.11			1.48	4.80		2.79	3.67			0.54	4.86	3.15	1.48	54.11	100.00
Spectrum 3	58.57		0.82	1.69		0.28		31.87		2.50	0.88	3.40				100.00
Spectrum 4	45.72		4.72	11.87				4.04			0.95	32.71				100.00
Spectrum 5	11.41		0.76	1.38		45.44		0.83			37.58	2.61				100.00
Spectrum 6	43.79		4.01	18.70				1.85			0.99	30.66				100.00
Spectrum 7	56.06		30.60	5.60				1.36	0.65		1.68	4.06				100.00
Spectrum 8	39.86		1.35	12.06				0.90			0.80	45.03				100.00
Spectrum 9	47.09	0.50	4.46	17.01				1.50			2.19	27.26				100.00
Max	58.57	0.50	30.60	18.70	4.80	45.44	2.79	31.87	0.65	2.50	37.58	45.03	3.15	1.48	58.67	
Min	11.41	0.50	0.76	1.38	4.64	0.28	2.43	0.83	0.65	2.50	0.54	2.61	1.99	1.48	54.11	

To determine the grain fineness of the original sample of oxidized zinc ore there was a sieve analysis using a set of sieves with the mesh sizes of 0.07; 0.1; 1; 4; 8 and 10 mm. The results of the sieve analysis are shown in Table 3.

Table 3. **The results of the sieve analysis of the oxidized ore sample,** *authors'*

Grain-size category, mm	Output, %				Zinc content, %
	Particular		Total		
	g	%	positive	negative	
+10	1356	38.74	0	100	20.29
-10+8	661	18.89	38.74	61.26	21.15
-8+6	169	4.83	57.63	42.37	20.08
-6+4	761	21.74	62.46	37.54	21.43
-4+2	3999	10.73	84.2	15.8	24.38
-2+1	544	1.72	94.93	5.07	24.0
-1+0.63	290	0.92	96.65	3.35	23.9
-0.63+0.315	328	1.04	97.57	2.43	24.1
-0.315+0.1	212	0.67	98.61	1.39	23.6
-0.1+0.074	90	0.44	99.28	0.72	23.6
-0.074+0	90	0.28	99.72	0.28	24.1
Total	8500	100	100	0	

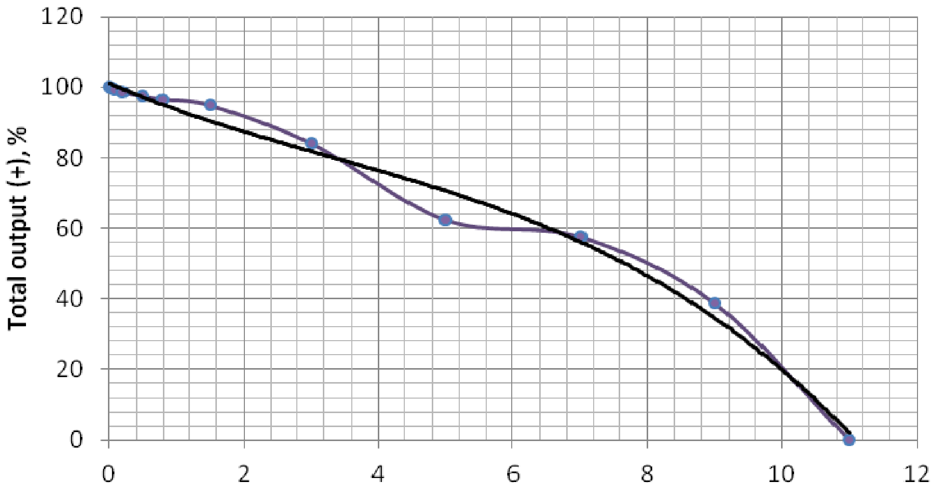

Figure 1. **Characteristics of the oxidized ore sample size,** *authors'*

On the basis of the sieve analysis results for "Shaimerden" oxidized ore samples we have built the characteristic size of the sample material (Figure 1) by the method of (Olevskiy, 1963).

Characteristic size of the oxidized zinc ore is convex in nature, showing the predominance of coarse grains. The content of fine grain size is low (sizes -0.1 + 0.074 and -0.074 + 0 mm) as it can be seen in Table 4.

Table 4 demonstrates that the coarse grains of the ore samples have lower zinc content than fine grains. At the same time, in coarse grain of the size (+2 mm), there are accumulated major mass fraction of zinc contained in the oxidized ore sample.

Table 4. **Distribution of zinc by grain-size category of oxidized zinc ore,** *authors'*

No.	Grain-size category, mm	Output, %	Content, Zn %	Distribution, Zn %
1	+10	38.74	20.29	35.11
2	-10+8	18.89	21.15	17.85
3	-8+6	4.83	20.08	4.33
4	-6+4	21.74	21.43	20.81
5	-4+2	10.73	24.38	16.48
6	-2+1	1.72	24.0	1.84
7	-1+0.63	0.92	23.9	0.98
8	-0.63+0.315	1.04	24.1	1.12
9	-0.315+0.1	0.67	23.6	0.71
10	-0.1+0.074	0.44	23.6	0.46
11	-0.074+0	0.28	24.1	0.31
	Total	100	22,39	100

Determination of the main parameter (sulfuric acid concentration) of one time direct leaching of the original sample of oxidized zinc ore, plus 2 mm grain size, was performed in a reactor with a stirring device.

Experiments on the oxidized zinc ore samples leaching were conducted in the following conditions:

– leaching temperature – 25^0C;

– leaching time – 1hour;

– the ratio of solids to liquid (*S:L*) – 1:4;

– concentration of sulfuric acid, *g/l* – 20, 30, 40, 50, 60, 65, 70, 75, 80, 85, 90, 95, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200.

A charge of ore in all experiments was 25 g.

Ore leaching experiments were carried out in the tank with the capacity of 0.5–0.6 dm, supplied the required volume of solvent (H_2SO_4). The ore was charged into the tank before supplying the sulfuric acid solution. During the leaching there was constant control over the amount of pulp in the tank. Rotation of the stirrer during the experiments was 220 rev/min. The temperature was recorded by the thermometer with the accuracy of ±1.00C.

At the end of the leaching slurry was filtered without preliminary condensation. Filtering the pulp was carried out in the funnel with 13 cm diameter through the "red belt" filter.

The solid phase (leaching cake) was washed on the filter from the filtrate residue; it was dried in the drying oven at 105^0C temperature till constant weight. Productive leaching solutions were analyzed for zinc content using the inductively coupled plasma mass spectrometry. Basing on the analysis results we have calculated zinc extraction into solution.

The extraction degree of controlled component (zinc) into productive solution depending on sulfuric acid concentration is presented in Table 5.

During the experiments we found the dependence of acid content of the oxidized zinc ore from "Shaimerden" deposit from the concentration of sulfuric acid (Figure 2). Taking into account the approximation and smoothing we obtained the polynomial trend line of the third degree, which has a linear character.

Table 5. **The extraction degree into the zinc productive solution depending on sulfuric acid concentration,** *authors'*

No.	*C* (H_2SO_4), g/dm^3	$V_{filtrate}$, g/dm^3	Content of *Zn*, g/dm^3	Content of *Zn* in the filtrate, g	Extraction degree into liquid phase, %	m_{cake}, g	Loss in weight, %
1	20	0.063	7.0	0.441	7.69	24.8910	0.44
2	30	0.056	10.5	0.588	10.25	24.7342	1.06
3	40	0.065	20.6	1.339	23.35	24.0931	3.63
4	50	0.056	25.0	1.400	24.41	24.5427	1.83
5	60	0.066	30.0	1.980	34.52	23.3431	6.63
6	65	0.065	34.0	2.210	38.54	23.2647	6.94
7	70	0.057	37.0	2.109	36.77	24.5017	1.99
8	75	0.069	43.0	2.967	51.73	24.1323	3.47
9	80	0.057	52.0	2.964	51.68	24.7926	0.83
10	85	0.062	55.0	3.410	59.46	23.5821	5.67
11	90	0.072	54.0	3.888	67.79	22.7804	8.88
12	95	0.065	56.0	3.640	63.47	22.7157	9.14
13	100	0.069	53.0	3.657	63.77	23.0826	7.67
14	110	0.063	58.0	3.654	63.71	23.0057	7.98
15	120	0.069	55.0	3.795	66.17	23.6561	5.38
16	130	0.070	54.0	3.780	65.91	23.5115	5.95
17	140	0.082	56.0	4.592	80.07	21.1352	15.46
18	150	0.078	57.0	4.446	77.52	20.8339	16.66
19	160	0.077	59.0	4.543	79.22	20.4724	18.11
20	170	0.078	61.0	4.758	82.96	20.6207	17.52
21	180	0.078	62.0	4.836	84.32	22.3809	10.48
22	190	0.072	60.0	4.320	75.33	23.7088	5.16
23	200	0.068	62.0	4.216	73.51	23.7958	4.82

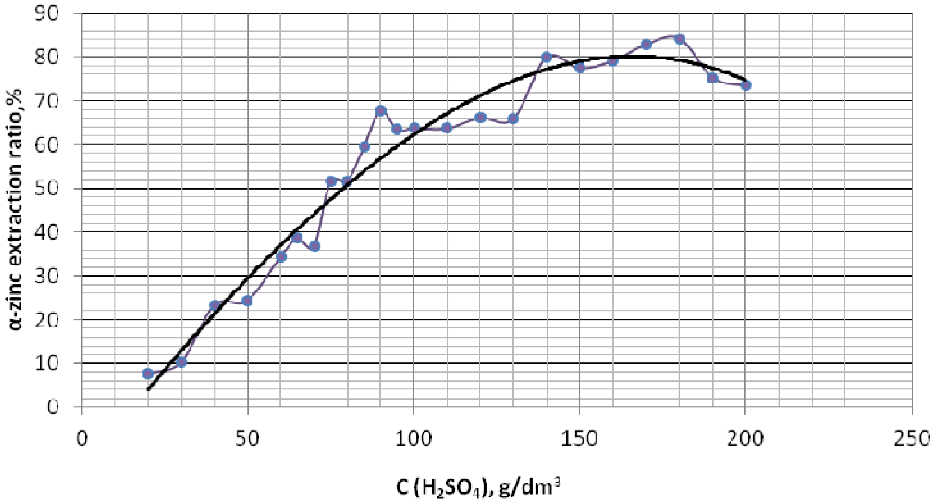

Figure 2. **Dependence of the zinc extraction degree and a productive solution from the concentration of sulfuric acid,** *authors'*

From Figure 2 it can be easily seen that there is an optimum concentration of sulfuric acid, which provides the maximum degree of extraction of the valuable component into a productive solution. It is evident that the best parameters are provided in the concentration range of sulfuric acid from 150 to 180 g/dm^3.

At the same time, the use of H_2SO_4 20–100 g/dm^3 concentrations leads to insignificant degree of zinc extraction into solution, it is apparently concerned with certain diffused difficulties, which are specific to solutions with insufficiently high concentration of solvent (Kolesnikov, 1981).

It is obvious, that the use of solutions with 20–100 g/dm^3 concentration of sulfuric acid is unpractical for zinc leaching. The use of solutions with more than 180 g/dm^3 concentration is also irrational, since it leads to reagent waste and does not lead to further increase in zinc extraction degree for more productive solution.

Increase of acid content in the ore can be explained by two factors – an increase of H_2SO_4 sorption capacity with the growth of its concentration and a more complete dissolution of the oxidized forms of ore minerals. The influence character of acid concentration growth on the reduction of ore solid mass is shown in Figure 3.

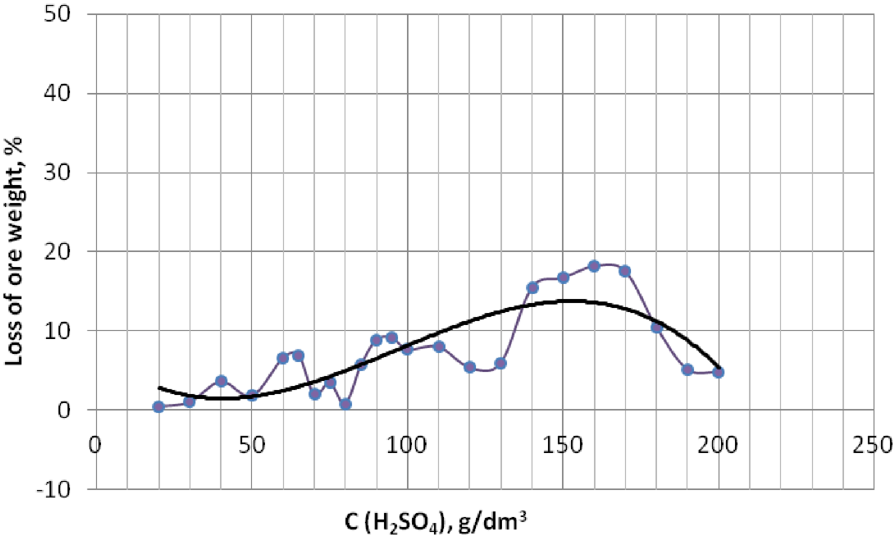

Figure 3. **The dependence of the ore weight loss from the concentration of sulfuric acid,** *authors'*

Our studies of sulfuric acid leaching of oxidized zinc ore and analysis of earlier performed work in this direction (Palenova, 2010; Kazanbayev, 2007; Tarasov, 2005; Tyan, 1992) allow us recommend a combined beneficiating and hydrometallurgical scheme of refractory zinc-containing raw materials processing as shown in Figure 4.

Extraction of zinc into sulphate solution under optimal conditions of ore leaching (Table 5) can be increased from 84% to 90% by reducing the fineness of the initial ore, washing of leaching cake and circulation of products in a closed circuit.

Similar processes of increasing the level of zinc extraction in the final product (the cathode zinc) previously mentioned by a number of authors (Tarasov, 2005), (Tyan, 1992), (Kazanbayev, 2007).

On the basis of conducted studies we calculated the consumption ratios of ore processing per 1 ton and analyzed technical and economic indicators of the proposed and the already known method of oxidized zinc-containing ores in order to produce commercial zinc in the amount of 100 ths t/year. The basic method involves the technological process stages of baking with roasted product production, Waelz process of zinc cakes, leaching of zinc oxide, electrolytic process to produce cathode zinc. The proposed method consists of leaching processes by a recommended scheme and electrolytic process. The calculations take into account the costs of preliminary preparation of raw materials for processing, namely crushing and enrichment.

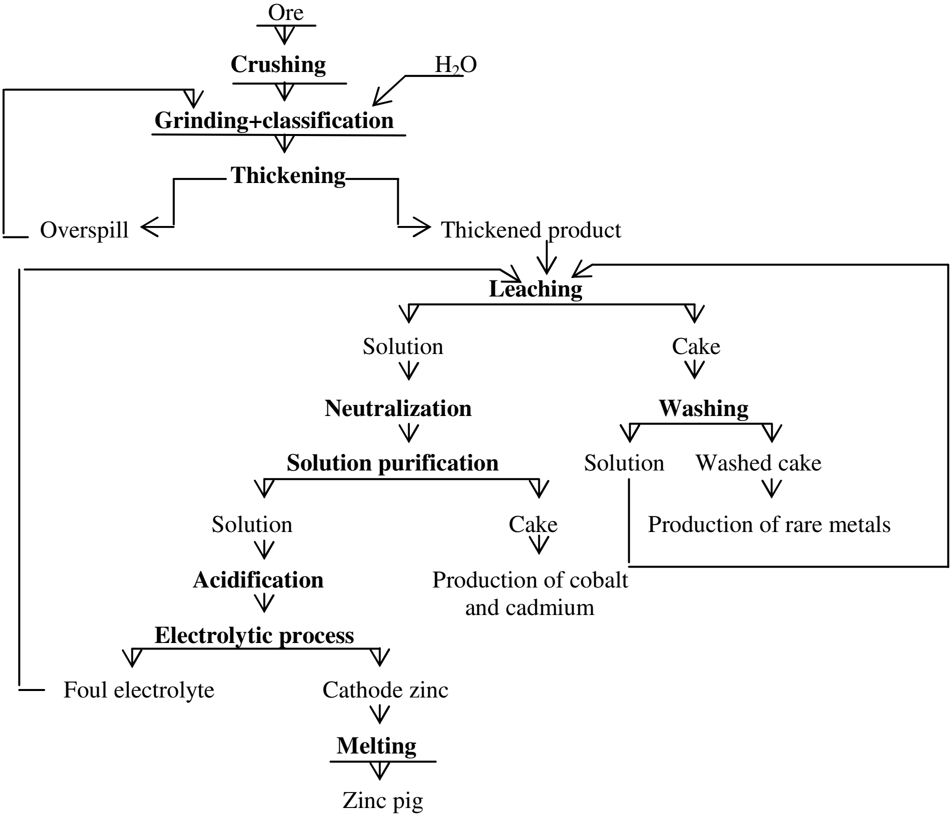

Figure 4. **Recommended scheme of oxidized zinc-containing ores processing,** *authors'*

The price of basic raw material – refractory oxidized zinc – containing ore of Shaimerden deposits is contractual. The price of the ore taken in the calculations is 12,000 tenge per 1 ton, but if we assume that the raw material is substandard the price of it can be much lower. Table 6 lists cost indicators for the proposed technology for 1 t of zinc from "Shaimerden" oxide ore deposit, as well as the annual output of zinc 100,000 t.

Table 7 shows the cost figures, profits from the current zinc production and from the method with the productivity of ore in 100 ths t of zinc per year proposed by the authors.

Table 7 shows that the cost of the proposed technology is much lower than the cost of the baseline technology. Cost reduction is 1.8 times.

Table 6. **Cost price of producing zinc from "Shaimerden" oxide ore deposit** (capacity of 100 ths t/year), *authors'*

Expenses	Unit price, USD	Expense per unit	Quantity	Total sum, USD
1. Raw material				
Ore, t	65.9		476,190.5	31,397,174.3
2. Auxiliary materials				
Sulphuric acid, kg	2.8	0.1300	61,904.8	173,469.4
Lime, kg	0.1	0.300	142,857.1	14,505.5
Zinc powder, kg	2.2	1.0000	476,190.5	1,043,772.9
Lining, kg	362.7	0.0001	47.6	17,273.3
Milling balls (D = 110–120 mm), t	349.2	0.0007	333.3	116,397.5
Milling balls (D = 40–80 mm), t	217.7	0.0006	285.7	62,192.7
Total materials and raw materials				32,824,785.6
3. Energy consumption technological expenses				
Electrical energy, kWh	0.1	8.19	3,900,000.0	212,571.4
Industrial water fresh water, m^3	0.1	2.000	952,381.0	57,561.5
Potable water, m^3	0.1	0.030	14,285.7	1,507.1
Total:				271,640.0
4. Expenses for labour payment				
Main staff, person	439.6	80.0		421,978.0
Auxiliary personnel, person	247.3	25.0		74,175.8
Engineering employee, person	659.3	20.0		158,241.8
TOTAL SALARY:				654,395.6
1. Earnings contribution				
Social tax., %		11		71,983.5
Expenses for labor protection, %		12.0		78,527.5
TOTAL:				804,906.6
5. Transport expenses, %		5		1,641,239.3
5.1. Other expenses, %		5		1,777,128.6
TOTAL PRIME COST:		373.2		37,319,700.0

Table 7. **Comparison of costs and profits of the base case and the suggested method of productivity of** 100 ths t of zinc per year, *authors'*

Expenses	Baseline technology, USD	Proposed technology, USD
Production costs		
1. Raw and auxiliary materials		
stage of baking	33,443,104.4	
stage of leaching	69,459,675.0	32,824,785.6
Waelz process	43,893,429.9	
stage of electrolytic process	114,746,166.7	114,746,166.7
2. Technological energy consumption		
stage of baking	725,536.3	
stage of leaching	124,069.0	271,640.0
Waelz process	211,035.7	
stage of electrolytic process	411,553.8	411,553.8
3. Labour costs		
stage of baking	654,065.9	
stage of leaching	407,034.5	804,406.6
Waelz process	238,836.3	
stage of electrolytic process	752,597.8	752,597.8
TOTAL PRIME COST:	265,067,105.3	149,811,150.5

Conclusions. As the result of our studies on the material composition of "Shaimerden" deposit oxidized zinc ore and optimization of its processing technology the following conclusions have been made:

1. The key specific features of material composition and oxidized zinc ore processing are determined:

- the nature of ore material fineness and distribution of zinc by separate grain-size categories;
- variety and complexity of the mineralogical and phase composition of ore samples;
- optimum concentration of the solvent (the concentration of H_2SO_4 is 160 c) during the process of ore material leaching;
- the conditions for ore leaching: concentration of of H_2SO_4 – 160 g/dm^3; temperature of the solution – 25^{0}C, leaching time – 1 hour;
- extraction of zinc into sulphate solution taking into account the washing of cake leaching – 95%.

2. Combined enrichment and hydrometallurgical technology for processing of oxidized zinc ore from "Shaimerden" deposit has been developed here. This technology provides throughout extraction of 90% of zinc from the ore.

3. The proposed technology of oxidized zinc ore processing provides a significant cost reduction in comparison with the baseline technology – 1.8 times.

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