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Earth sciences

Improvement of the technological scheme for processing zinc concentrates by hydrometallurgical method at JSC Almalyk MMC

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ABSTRACT
The extraction of zinc from concentrates is carried out in pyrometallurgical and hydrometallurgical ways. Obtaining pure zinc of the highest grades is possible using the hydrometallurgical method, in which the calcined sulfide concentrate is subjected to sulfuric acid leaching, a solution of zinc sulfate and a recycled product is formed - a solid residue of the cake leaching process. After purification, the zinc sulfate solution is subjected to electrolytic refining, and the cake is processed pyroly or hydrometallurgically. At JSC "Almalyk MMC" in the process of hydrometallurgical processing of zinc concentrates, the resulting zinc cake is processed by the pyrometallurgical method - rolling. The rolling process takes place in two tubular furnaces (rolling furnaces) 50 meters long and 3.5 meters in diameter at a temperature of 1100–1200^{0}C, in the presence of a reducing agent, coke breeze and petroleum coke. As a result of the rolling process of zinc cakes, sublimates and a solid technogenic residue, clinker, containing copper, gold, and silver are formed. Clinker is processed at the plant in smelting furnaces to extract precious metals, but it is accumulating more than 450 thousand tons. In connection with this, scientific research is currently underway on the processing of zinc cakes using a hydrometallurgical method to eliminate the expensive rolling process of processing zinc cakes; high-temperature (90^0 C**)** sulfuric acid leaching of cakes with a size of 0.074 mm has been developed during leaching for 4-4.5 hours, the extraction of zinc into the solution is 98.5%; copper 92.8%; iron 75.2; cadmium 79.2.
Keywords: zinc, cake, process, leaching, concentrate, cinder, extraction, solution, clinker, coke.

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Introduction

Zinc can be extracted from concentrates in two ways: pyrometallurgical (distillation) and hydrometallurgical (electrolytic). Historically, the first method was pyrometallurgical; two thousand years BC in India they knew a method for obtaining zinc from ore; in Europe only at the end of the 18th century.

Zinc sulfide raw materials can be directly reduced to produce zinc metal:

$$Zn\,S + H_2 = Zn + H_2S$$

The equilibrium constant of the given reaction at a temperature of 1000 ° C is insignificant; even at a the high value *of* P_{H2}, the yield of reduction products is low [1].

In this connection, it is more rational to carry out separately the oxidation of Zn S (roasting) and the reduction of oxidized zinc to metal. The technology of the method and the hardware design of the process are associated with the peculiarities of the reduction of zinc from oxide, to the metal with carbon and CO occurs at a temperature of 1,000–1,100 ° C, and the boiling point of the resulting zinc is 907 ° C. Advantages The pyrometallurgical scheme is its few stages, high direct extraction of zinc into metal, high productivity of continuous equipment and the ability to process low-quality raw materials. Flaws This scheme means a high consumption of coke, a low complexity of the use of raw materials and the production of zinc of lower grades, and currently in world practice no more than 15% of zinc is obtained using the pyrometallurgical method. This technology is usually used to process poor zinc concentrates with high impurity content [[1], [2]].

Much attention is paid to more complete extraction of the components of zinc-containing raw materials, obtaining pure zinc of the highest grade, and therefore in the production of zinc, the hydrometallurgical method of processing zinc concentrates is currently used, it is also used at Almalyk MMC JSC. In this method (zinc cinder leaching process), maximum extraction of zinc into the zinc sulfate solution occurs and the solid tail of the leaching process is the recycled product zinc cake. The solution after cleaning is transferred to Electra of zinc precipitation, and zinc cake containing 20-23% Zinc is processed using the pyrometallurgical method - the Waelz process.

The Waelz process gives high zinc yields of more than 90-93%, but it is quite expensive due to the high consumption of coke, about 50% of the weight of the zinc cake. As a result of the Waelz process, zinc sublimations are obtained, as well as man-made waste from zinc production, difficult to recycle clinker with a high content of non-ferrous and precious metals, carbon and iron [2].

Clinker from zinc production is mainly processed by smelting in shaft furnaces, the negative side of smelting is the expense of an expensive reducing agent - coke, as well as briquetting or pelletizing of clinker for processing in shaft furnaces [[3], [4], [5], [6]].

Clinker is also processed in a reverberatory furnace, mixing it with concentrate and fluxes, it is loaded into the furnace to extract only noble (gold, silver) metals, and during the smelting process, the elements contained in the clinker carbon are burned aimlessly, and the iron goes into waste slag [[7], [8], [9]].

Scientific research is being conducted around the world on the processing of zinc cakes using the hydrometallurgical method, in order to eliminate the use of expensive coke in the Waelz process. The hydrometallurgical method mainly uses technology that includes: two-stage leaching, the first stage is neutral leaching of Waelz oxides, and the second is acid leaching of the solid residue after neutral leaching [[10], [11], [12], [13], [14], [15], [16]].

The authors of used a promising method - cation exchange leaching of metals from zinc cinder and zinc cake (obtained at the stage of acid leaching), in which the KU-2–8 ion exchanger in the H-form can be used as a reagent, allowing the extraction of 98% of zinc of the total [17].

The authors of developed a technology for processing clinker, waste from zinc production, to produce ferroalloy and sublimates of non-ferrous metals [18]. Clinker from zinc production was used as a raw material to obtain commercial products in the form of ferrosilicon and collective sublimates of non-ferrous metals. The degree of extraction of silicon into the ferroalloy was up to 96%, Fe up to 97%, and in sublimation Zn 99.6%, Pb – 99%.

In work, the Institute of JSC "Uralmekhanobr" developed a technology for enriching clinker of JSC "Electrozinc" by gravity-magnetic-flotation processing to produce carbon-containing concentrate, iron concentrate with a high copper content [19].

The work presents the results of studies on the use of flotation for the enrichment of zinc cakes [20]. The concentrate of the second cleaning contained, %: 44 Zn; 9.3 Fe; 1.5 Cu; 1.1 Pb; 0.88 Ag; 0.009 Au; 2.1 SiO_2 and 27.3 S.

The authors of claim that sodium sulfide used in flotation does not always ensure complete sulfidization of the surface of minerals [21]. Studies of the flotation process on the original product and after preliminary sulfidization by a pyrometallurgical method have found that in the preliminary sulfidation of the product, the extraction of zinc will increase by 17.23%, and lead by 10.07%, compared to the original product without pretreatment.

Authors a method has been developed for processing technogenic waste, which reduces specific fuel consumption by 1.5-1.7 times and increases specific productivity by 1.4-1.5 times. The industrial implementation of the “phase inversion reactor-tubular furnace” unit would make it possible to cost-effectively process slag dumps from the Shymkent lead plant, Waelz clinker , “poor” zinc ores from the Achpolimetal plant, tailings from the Tekeli Mining and Metallurgical Plant and other non-ferrous metallurgical facilities [[22], [23], [24], [25], [26]].

The results of a study of the process of sulfatizing roasting of zinc cakes of PJSC Chelyabinsk Zinc Plant using iron sulfates $FeSO_4$ and $Fe_2(SO_4)_3$ are presented. In laboratory experiments, it was found that from fired samples, no less than 98% of zinc and no less than 88% of copper goes into solution during water washing, while the degree of iron transfer into solution does not exceed 3% [[27], [28], [29]].

An analysis of the processing of zinc production cakes showed that the technological schemes are quite complex, expensive and complete extraction of

Table 1 - Mineralogical composition of zinc cake, %

Product name	Connections, %					
	Zntot	$ZnSO_4$	ZnO	ZnO SiO_2	ZnS	$ZnFe_2O_4$
Zinc cake	21.42	7.97	3.05	3.44	1.07	6.11
	$CuFe_2O_4$	$CuSO_4 \cdot 5H_2O$	Cu_2S	CuO	CdO	$CaSO_4 \cdot 2H_2O$
	5.25	1.45	0.16	0.03	0.02	7.16
	$PbSO_4$	FeS	Fe_2O_3	$CaCO_3$	MnS	MgO
	6.05	1.27	0.56	1.45	1.28	0.45

Table 2 - Chemical composition of zinc cake by fractions

Class, mm	Class yield, %	Content, %							
		Zn	Cu	Pb	Cd	Fe	Al_2O_3	SiO_2	S
+40	1.925	21.89	3.27	6.48	0.22	17.23	4.11	9.23	7.77
-40+20	11.35	21.60	3.38	6.57	0.22	17.34	4.13	9.18	7.75
-20+10	30.35	21.08	2.35	6.52	0.20	16.48	4.08	9.14	7.66
-10+5	32.25	21.62	2.34	6.49	0.21	16.50	4.15	9.36	7.69
-5+2	20.8	21.66	2.23	6.37	0.20	16.66	4.12	9.29	7.71
-2+1	0.7	21.63	3.33	6.25	0.29	14.60	4.07	9.17	7.74
-1+0.315	0.75	21.95	3.37	6.32	0.29	13.75	4.08	9.19	7.65
-0.315+0.140	0.5	22.45	2.29	6.32	0.28	12.09	4.17	9.14	7.68
-0.140	1.375	21.66	2.08	6.39	0.28	12.07	4.18	9.16	7.73

metals is not achieved. In this connection, there is a need to develop a more efficient technology for processing zinc production cakes, one of which is high-temperature leaching.

Objects and methods of research

Cake was taken from the Zinc Plant of Almalyk MMC JSC, %: Zn_{total} -21.42, Zn_{aq} -5.59, Zn_{acid} -13.26, C -0.14, S_{vol} -7, 69, S_{SO4} -6.86, Pb-6.48, Fe-15.21, SiO_2 -9.39, Al_2O_3 -1.42, Cu-2.32, Cd-0.21, CaO-2.67, MnO-0.85, As-0.35. The main chemical compounds of zinc cake are sphalerite, zinc ferrite, copper ferrite, metal silicates, copper sulfate, zinc sulfate, gypsum and sphalerite, and lead sulfate. The mineralogical and fractional composition of zinc cake using spectral, chemical and mineralogical methods of analysis are given in Table. 1-2.

Methodology for high-temperature leaching of zinc cake

To study the process of agitated high-temperature leaching of both preparative reagents and bulk products, a special LR 1000 basic unit was used.

The experiments were carried out as follows: the zinc product was crushed to a fraction of <0.1 mm. A crushed sample of zinc cake was placed in a leaching unit, and a solution of sulfuric acid was added, heated and held for a certain time. The temperature was regulated through a microprocessor automatic controller. Pulp samples for analysis were filtered through a paper filter with a blue ribbon, and the filtrate was analyzed for iron, zinc, copper and other components. After completion of the experiment, the phases were separated by filtration, the cake was washed three times by decantation with hot water (50^0C), dried to constant mass and subjected to atomic absorption and X-ray analysis for the content and form of metals.

LR 1000 basic laboratory reactor designed to optimize the reproduction and optimization of chemical reaction processes, as well as for mixing at different temperatures, dispersion, homogenization on a laboratory scale. The temperature of the processed material can reach 120ºC. The temperature of the heating source located under the vessel is adjusted by the set temperature inside the medium. Digital display allows you to clearly monitor speed and temperature.

Discussion of the research results

A study of the influence of the dependence of zinc extraction into solution on temperature at various concentrations of sulfuric acid, the duration of the process on the leaching of zinc from cake with a sulfuric acid solution with a concentration of 120-210 g/l, at various temperatures shows that at the beginning of the process 1 - 1.5 hours, zinc extraction in the solution flows efficiently, and after 4–5 hours the equilibrium of the leaching process is established (Fig. 1-2).

An increase in the duration of the process leads to a decrease in the concentration of sulfuric acid, while the iron content in the solution increases (Fig. 3).

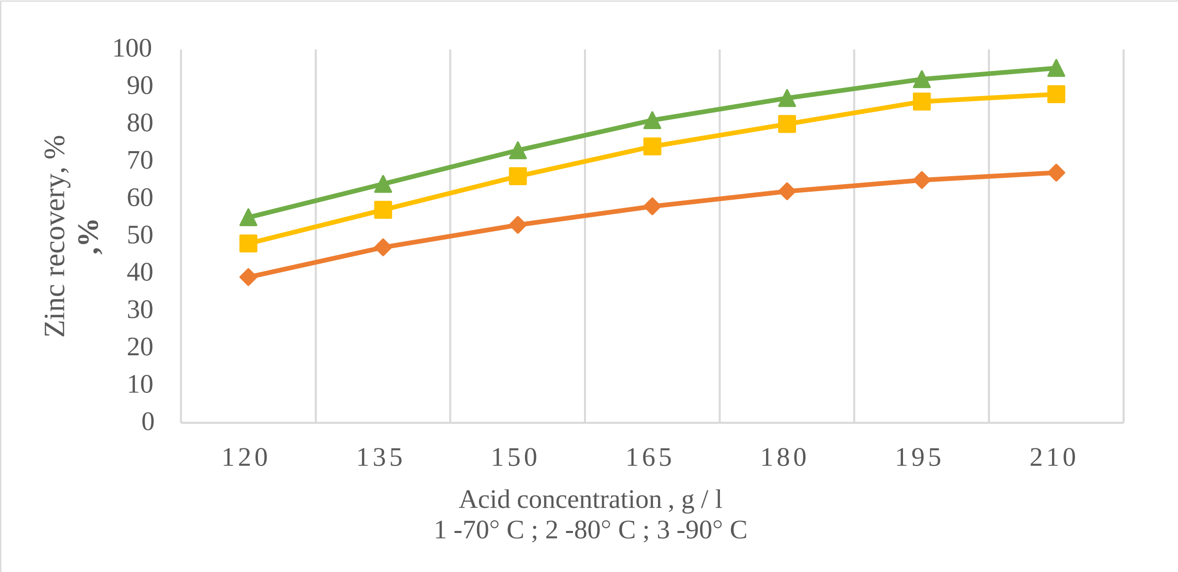

Fig.1 - Extraction of zinc from cake during zinc cake leaching process which depends on temperature.

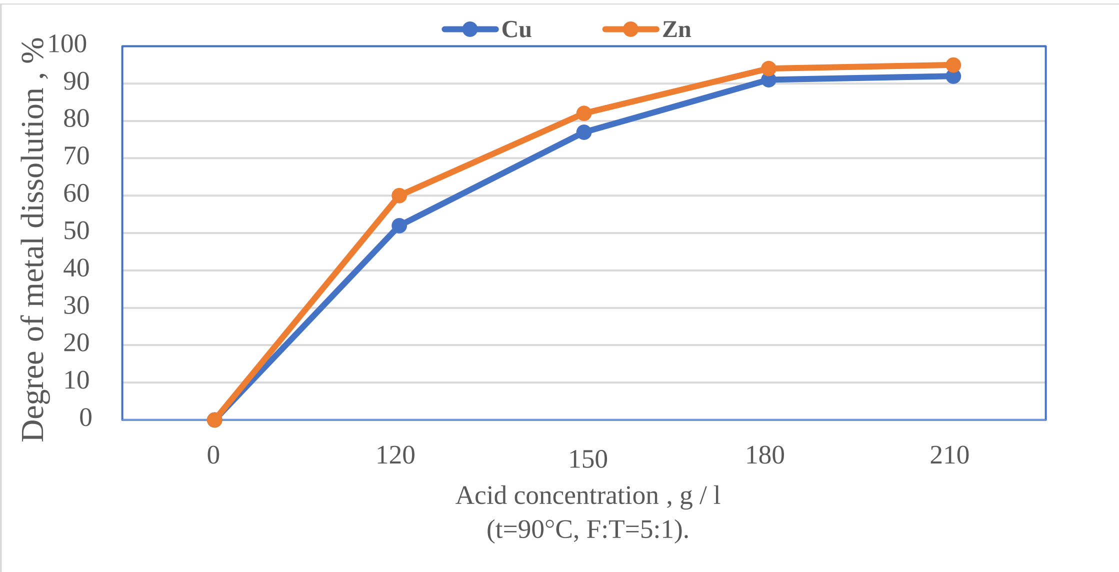

Fig. 2 - The degree of zinc and copper`s dissolution during the process of zinc cake`s leaching at 90 ˚C depending on the concentration of sulfuric acid

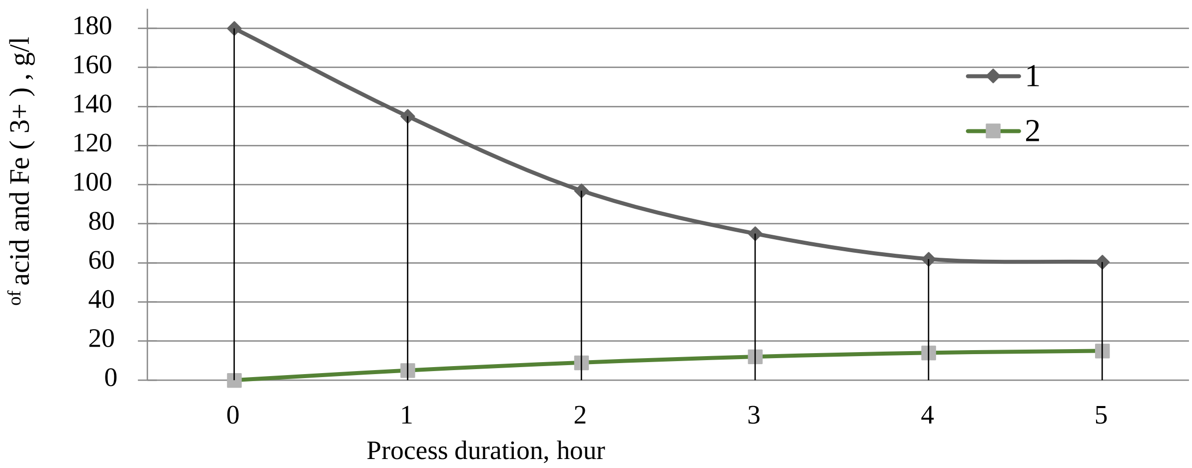

Fig. 3 - Dependence of the change in the concentration of sulfuric acid (1) and iron (2) on the duration of the process

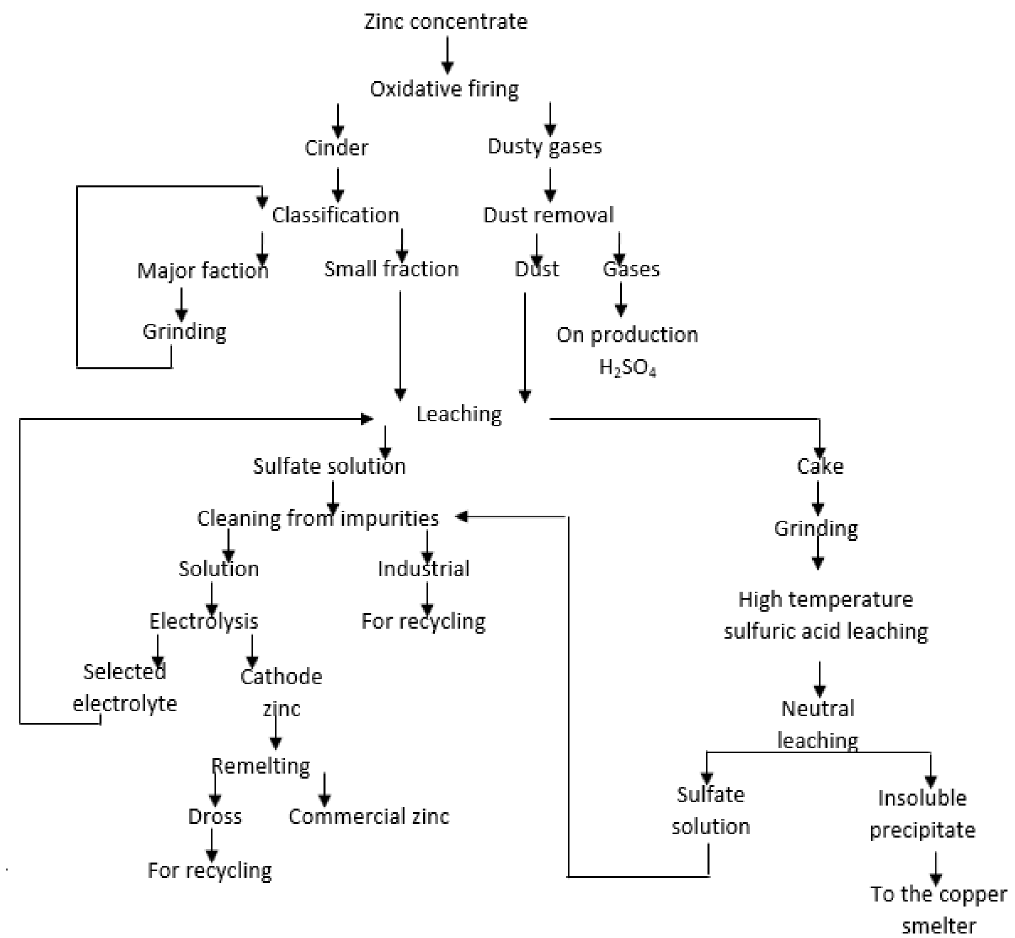

Fig. 4 - Improved technological scheme for processing zinc concentrates by hydrometallurgical method.

To clean the high-temperature sulfuric acid leaching solution from copper, cadmium, cobalt, antimony, nickel and other impurities, three-stage neutral leaching with zinc dust is carried out in mixers with mechanical stirring. The resulting sediment (copper cake) is transferred to cadmium production.

In the improved technological scheme for processing zinc concentrates using the hydrometallurgical method, Figure 4 shows a section in the scheme of processing zinc cakes using a high-temperature sulfuric acid leaching process.

In Figure 4 shows a scheme for processing zinc cakes using a high-temperature sulfuric acid leaching process, instead of the Waelz process used in many zinc plants around the world.

Thus, the following optimal conditions for leaching zinc cake were established: sulfuric acid concentration 180–190 g/l, temperature 90 ^{0} C, duration 4–4.5 hours. Under these conditions, the degree of extraction of zinc into solution is 97–98.5%, copper 92–93%, cadmium 78–80% and iron 72.5–75.2%. In the resulting sulfate solution, the concentration of zinc in the solution is sufficient to transfer it to the zinc electrolysis workshop; the impurities contained in the solution are first purified by the hydrolytic method used at the zinc plant of Almalyk MMC JSC.

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Conflicts of interest. On behalf of all authors, the correspondent author declares that there is no conflict of interest.

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«Алмалық ТМК» АҚ-да мырыш концентраттарын гидрометаллургиялық әдіспен өңдеудің технологиялық сызбасын жетілдіру

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ТҮЙІНДЕМЕ
Концентраттардан мырыш алу пирометаллургиялық және гидрометаллургиялық әдістермен жүзеге асырылады. Ал жоғары сортты мырыш гидрометаллургиялық әдісті қолдану арқылы алынады, онда күйдірілген сульфид концентраты күкірт қышқылды мырыш ерітіндісімен күкірт қышқылды шаймалауға ұшырайды, нәтижесінде қайта өңдеу өнімі – қоқымды (сүзіндіні) шаймалау процесінің қатты қалдығы түзіледі. Тазартудан кейін мырыш сульфаты ерітіндісі электролиттік тазартуға ұшырайды, ал қоқым пиро - немесе гидрометаллургиялық жолмен өңделеді. «Алмалық ТМК» АҚ-да мырыш концентраттарын гидрометаллургиялық өңдеу процесінде алынған мырыш қоқымын пирометаллургиялық әдіспен – илектеу арқылы өңдейді. Илектеу процесі ұзындығы 50 метр және диаметрі 3,5 метр екі құбырлы пеште (илектеу пеші) 1100–12000^{0}C температурада, тотықсыздандырғыштың, кокс ұсағының және мұнай коксының қатысуымен өтеді. Мырыш қоқымын илектеу нәтижесінде возгондар мен қатты техногендік қалдық, құрамында мыс, алтын, күміс бар клинкер түзіледі. Клинкерден қымбат металдарды алу үшін, ол зауытта балқыту пештерінде өңделеді. Қазір 450 мың тоннадан астам клинкер жинақталып тұр. Осыған байланысты қазіргі уақытта мырыш қоқымдарын өңдеудің қымбат илектеу процесінің орнына, гидрометаллургиялық әдіспен мырыш қоқымдарын өңдеу бойынша ғылыми зерттеулер жүргізілуде. 4-4,5 сағат шаймалау кезінде мөлшері 0,074 мм қоқымдарды жоғары температурада (9000^0 C) күкірт қышқылымен шаймалау игерілді, ерітіндіге мырыштың алынуы 98,5% құрайды; мыс 92,8%; темір 75,2%; кадмий 79,2% болады.
Түйін сөздер: мырыш, қоқым (сүзінді), процесс, шаймалау, концентрат, қож, экстракция, ерітінді, клинкер, кокс.

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Совершенствование технологической схемы переработки цинковых концентратов гидрометаллургическим способом на АО «Алмалыкский ГМК»

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АННОТАЦИЯ
Извлечение цинка из концентратов осуществляется двумя способами: пирометаллургическим и гидрометаллургическим, а получение чистого цинка высших марок возможно гидрометаллургическим методом, при котором прокаленный сульфидный концентрат подвергают сернокислотному выщелачиванию раствором сернокислого цинка и образуется рециркуляционный продукт – твердый остаток процесса выщелачивания кека. После очистки раствор сульфата цинка подвергают электролитическому рафинированию, а кек перерабатывают пиро- или гидрометаллургическим способом. На АО «Алмалыкский ГМК» в процессе гидрометаллургической переработки цинковых концентратов полученный цинковый кек перерабатывается пирометаллургическим методом – прокаткой. Процесс прокатки происходит в двух трубчатых печах (прокатных печах) длиной 50 метров и диаметром 3,5 метра при температуре 1100-12000С, в присутствии восстановителя, коксовой мелочи и нефтяного кокса. В результате прокатки цинковых кеков образуются возгоны и твердый техногенный остаток — клинкер, содержащий медь, золото и серебро. Клинкер перерабатывается на заводе в плавильных печах с целью извлечения драгоценных металлов, но на данный момент его накапливается более 450 тысяч тонн. В связи с этим в настоящее время проводятся научные исследования по переработке цинковых кеков гидрометаллургическим методом с целью исключения дорогостоящего прокатного процесса переработки цинковых кеков; освоено высокотемпературное (900 С) сернокислотное выщелачивание кеков размером 0,074 мм при выщелачивании в течение 4-4,5 часов, извлечение цинка в раствор составляет 98,5%; медь 92,8%; железо 75,2%; кадмий 79,2%.

Ключевые слова: цинк, кек, процесс, выщелачивание, концентрат, огарок, экстракция, раствор, клинкер, кокс.

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