



ISSN: 2350-0328

**International Journal of Advanced Research in Science,
Engineering and Technology**

Vol. 6, Issue 4, April 2019

Thermodynamic Analysis of Reactions Proceeding During Electrical Leading Zinc Production Clinker

ABDURAXMONOV SOIB, TOSHKODIROVA RANO, KHOLIQULOV DONIYOR

Professor of Department of Metallurgy, Tashkent state technical university Almalyk branch,
Dr.Sci.Tech., professor, Almalyk, Uzbekistan;

Senior teacher Department of Metallurgy, Tashkent state technical university Almalyk branch, Almalyk, Uzbekistan;
Deputy Director for Research and Innovation Almalyk branch of the Tashkent state technical university, PhD, associate
professor, Almalyk, Uzbekistan;

ABSTRACT: The paper presents the results of studying the chemical, mineralogical and granulometric composition of zinc clinker. The thermodynamics of various reactions occurring during electroleaching has been studied.

KEYWORDS: clinker, cake, zinc, thermodynamics, reaction, electroleaching, ion, solution, light fraction, composition.

I. INTRODUCTION

There are few states on the world map that would possess such wealth that the land of Uzbekistan has. The rapid pace of development of all industries in the conditions of independent Uzbekistan leads to the increase of output of mineral raw materials.

Along with natural minerals, industrial wastes of metallurgical production are also of considerable interest. These wastes include clinker, which contains significant amounts of gold, silver and copper. Clinker from the manufacture of zinc cakes is one of the largest and most valuable waste of zinc production. From the moment of operation of the AMMC zinc plant, an enormous technogenic deposit has emerged. About 500000 tons of clinker containing gold, silver, copper, zinc, lead and coke has accumulated there. The annual increase is 25000-30000 t. Accumulation of clinker is caused by irreparable damage to the environment due to the penetration into the soil and hydrosphere of heavy metal ions (copper, zinc, cadmium, lead, arsenic) and other toxic substances.

II. SIGNIFICANCE OF THE SYSTEM

The main attention in the article is paid to the object of the research - to clinker, waste of zinc production and a possible method of its processing. Clinker is a mechanical mixture of carbon with minerals which are mutually closely associated with each other. They cannot be separated by methods of enrichment, because components are distributed across all products. For the same reasons, repeated attempts to create combined schemes based on preliminary separation from the clinker by the methods of mechanical enrichment of concentrates and industrial products of copper, iron and precious metals with their subsequent pyrometallurgical processing were not crowned with success. In the world practice of processing of zinc production, the pyrometallurgical method of clinker processing has been widely used. The methods of clinker processing are based on pyrometallurgical techniques, had all the disadvantages inherent in pyrometallurgy. First of all, it is necessary to notice high energy intensity, i.e. the need for energy to melt the entire mass of clinker at a temperature of 1273-1473K, and the inevitable environmental pollution due to dust and gas emissions and slag dumps. The addition of clinker to sulphide-containing raw materials using autogenous smelting was also unsuccessful, because it does not effectively extract valuable components and is accompanied by the formation of a large volume of low-sulfur (0.1-5 %) waste gases that are unsuitable for cost-effective disposal and require unreasonably high costs for gas cleaning and dust collection. In addition, in these cases, noble metals were not removed as finished (marketable) products, but turned out only in the form of industrial products that were transferred for further processing.



ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 6, Issue 4, April 2019

The authors of the work carried out studies on the study of the chemical, mineralogical and granulometric composition of clinker, with the aim of obtaining initial data to select the direction of further technological research for processing.

Worked out technology allows:

- clinker processing by electrochlorination using magnetic enrichment;
- the use of electrochlorination with magnetic enrichment allows complex extraction of valuable components that are present in the composition of clinker, to separate the iron concentrate, carbon, non-ferrous and precious metals.

The scientific and technical solution of the problem posed by this problem is to create a technology for extracting valuable components from zinc production clinker.

III. LITERATURE SURVEY

S.M. Anisimov et al. Developed a combined clinker enrichment scheme using jigging and subsequent magnetic separation or flotation of concentrate. Experiments were conducted on the direct flotation of clinker, however, due to the high consumption of reagents and other difficulties, this direction was considered not promising [1].

Studies on the gravitational enrichment of clinker were conducted at ElectroZinc OJSC of the Ural Mining and Metallurgical Company. An important drawback of the scheme is that it is necessary to use machines with a device for continuous unloading of oversize concentrate for jigging, which significantly complicates the reliability of work and increases their cost [2].

Studies have been carried out and a patent was obtained [3] "Method of processing waste of zinc production". According to the proposed method, the clinker is crushed to a particle size of 1-5 mm and subjected to magnetic separation. The disadvantages of the method are multistage, i.e. for carrying out, several methods are needed at once, and as a result, all the same, cakes after heap leaching are subjected to smelting in a furnace.

The enrichment of clinker in the heavy suspension is implemented at the plant. D. Blagoeva (Plovdiv). The technological scheme includes screening operations on a sieve with hole sizes of 16 mm, enrichment of the fine fraction (<16 mm) in heavy suspension and magnetic separation of the heavy fraction. The resulting intermediates were partially processed into electric furnaces [4].

At the State Enterprise "Central Laboratory" of the State Committee of the Republic of Uzbekistan on Geology and Mineral Resources, research was conducted on the processing of zinc clinker produced by JSC "Almalyk MMC". The authors have developed a new method that includes low-temperature sulfatizing clinker burning, which allows transforming "refractory" minerals into soluble sulfate copper and zinc salts, which are selectively extracted into the solution in the form of stable ammoniate $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ and $\text{Zn}(\text{NH}_3)_4\text{SO}_4$. It is necessary to separate copper and zinc from solution, fractional crystallization. Questions on the extraction of other metals are not fully considered. Different options are offered, but there are no concrete results [5].

Analysis of the reviewed literature and practice of existing enterprises on the problem of processing zinc production clinker allows conducting research in the following direction:

- the study of chemical, mineralogical and granulometric composition of zinc production clinker;
- comparison of technological parameters obtained during the experiments;
- the choice of the optimum mode of leaching of clinker.

In addition, it is necessary to study and select the technology for the extraction of metals from solutions.

IV. METHODOLOGY

Study of the chemical, mineralogical and granulometric composition of zinc production clinker. On a sample of clinker, studies were carried out to study the material and chemical composition, as well as a mineralogical description of minerals. The results of the chemical and mineralogical composition of zinc clinker production using chemical, mineralogical and particle size analysis methods are given in Tables 1-3.

Studies on the study of particle size distribution. Sieve analysis. The study of particle size distribution was performed by sieve analysis by mixing the sample with a particle size of 20 mm in a cylindrical container for 15 minutes, followed by sieving of each size class. The obtained size classes were subjected to cutting with sampling for chemical analysis, in which the content of metals was determined. The particle size distribution of the original clinker is shown in Table 3.

According to the phase analysis, the main forms of zinc in clinker are: sulfide (45 %), silicate (17 %), ferrite (20 %) and oxide (18 %), lead in the clinker is contained in the following forms: metal (40 %), sulfide (29 %), aluminate (25 %), oxide and silicate (6 %), copper is mainly represented by sulfide (bornite). The degree of metallization of copper is 22-32 %. Iron in clinker is present in the form of sulphides, but the main form is represented by metallic iron. The degree of metallization of iron is 80-90 %. Part of iron in the form of oxides is bound to ferrites and silicates.

From tables 1-3 it is visible that zinc, copper, lead, cadmium, iron, noble metals, etc. are of industrial interest for the extraction of metals.

Table 1. The chemical composition of clinker, %

Product name	Content, %																	
	Cu	Pb	Zn	Cd	Fe _{06III}	As	S _{06III}	C	Ba	H ₂ O	Au, g/t	Ag, g/t	SiO ₂	CaO	MgO	Al ₂ O ₃	Mn ₂ O ₃	TiO ₂
Clinker of zinc production	2,2	0,51	2,1	0,01	19,53	0,155	8,39	29,55	2,3	0,6	3,2	260,27	16,42	6,06	2,72	4,08	0,47	0,21

Table 2. The results of phase analysis of clinker

Substance	Copper content, %	Copper distribution by compounds
Secondary copper sulfides	1,91	89,7
Chalcopyrite	0,16	7,5
Metallic copper	0,01	0,5
Copper ferrite	0,05	2,3
Amount	2,13	100

Table 3. Granulometric composition of the original clinker ACZ

Sample number	Fraction distribution									
	Size fraction, mm	+20	-20+10	-10+6	-6+2	-2+1	-1			Total
1	Quantity, %	20,5	20,3	25,4	17,7	14,3	1,5			100
	Quantity, %	22,5	21,6	25,2	11,3	2,5	13,5	1,9	1,5	100

According to the particle size analysis of the clinker of the Almayk zinc plant (table 3), the clinker consists mainly of large fractions. The class of +20 mm is from 20 to 23 %, the class of -20 + 10 mm is from 20,3 to 21,6 %, the class with a particle size of -10 + 6 mm is 25,2-25,4 %, the class is -6 + 2 mm from 11,3-17,7 %. Small classes are distributed -2+ 1 mm from 2,5-14,3 %, -2 + 1 mm 1,5-1,9 %, class-0,5 mm 1,5 %. From here we can draw the following conclusions; before processing, clinker must be prepared for subsequent processing by crushing, grinding and other methods to a particle size of -1,0 mm.

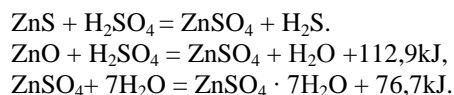
V. EXPERIMENTAL RESULTS

Let us analyse the specific and most important tasks for the technology of clinker processing by the hydrometallurgical method. The analysis of the behavior of the components of clinker in sulphate solutions.

Zinc compounds. Zinc sulfate (ZnSO₄) is easily soluble in water and no acid is consumed on it. Therefore, a high (above normal) content of sulfate sulfur in clinker leads to an increase in the content of zinc sulfate in the solution, and, as a consequence, to an increase in the density and viscosity of the solution, which causes deterioration of sedimentation and imbalance of sulfuric acid in a closed production cycle.

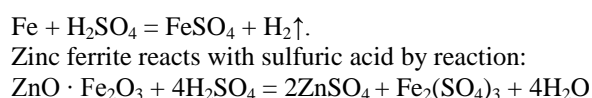
Zinc ferrite (ZnO·Fe₂O₃) dissolves in weak sulfuric acid is much more difficult than zinc oxide. A high concentration of sulfuric acid (200 g / dm³ or more) and elevated temperature (353-363 K) are necessary to transfer zinc into the solution from ferritic compounds. In these conditions, along with zinc, a large amount of iron (III) passes into the solution.

In dilute solutions of sulfuric acid, zinc sulfide ZnS practically does not dissolve. In strong acid and at high temperature, it reacts with the solvent to form hydrogen sulfide by the reaction



Usually, 85 - 90 % of zinc from its content in clinker can be transferred to the solution.

Iron compounds. The main amount of iron in clinker is in metallic form, partly in the form of sulphides of zinc, copper, cadmium and other metals. Metallic iron reacts with sulfuric acid by reaction

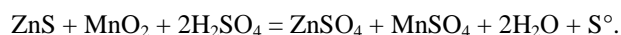


Total in the solution passes 60-65 % of iron from its content in the clinker.

Free-form silica does not interact with sulfuric acid, but, being bound to lead and zinc oxides in silicates, easily goes into solution.

Silicic acid is very slightly soluble ($\sim 0,2\text{g} / \text{dm}^3 \text{SiO}_2$), but goes into solution in the form of sols, forming colloidal solutions.

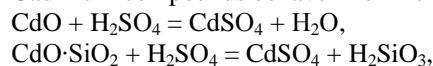
Zinc sulfide does not dissolve during leaching; however, in the presence of an oxidizing agent, iron (III) sulfate or manganese dioxide, introduced for the oxidation of iron, goes into solution due to the reaction:



As a result, the extraction of zinc in the solution increases.

Cadmium compounds. Cadmium is mainly in the form of oxide and in very small quantities in the form of sulphate, silicate, ferrite and sulphide.

Cadmium compounds behave like zinc compounds. As a result of the reactions



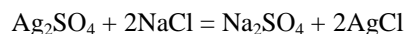
up to 70 % of cadmium from its content in the clinker is transferred into the solution. Ferrite and cadmium sulfide in weak sulfuric acid are insoluble.

Copper compounds. In clinker, copper is mainly in the form of CuO, CuSO₄, CuO·Fe₂O₃ and CuO·SiO₂. When leaching in the first place, sulfate and copper oxide dissolve easily, resulting in 50 - 60 % of this metal goes into solution. Copper ferrite is practically insoluble in weak sulfuric acid and remains in the cake.

When leaching, up to 70 - 75 % of copper, clinker is usually transferred to the solution.

Gold does not dissolve in weak sulfuric acid and remains in the cake.

Silver sulphate is easily soluble. In the presence of chlorine ions forms by reaction



poorly soluble compound - silver chloride, which turns into a solid residue.

Most of the lead remains in the cake in the form of sulfate. However, 1-3 mg / dm³ of lead is always present in the solution.

Calcium and barium compounds. When leaching calcine carbonates and oxides of calcium and barium are converted to sulfates.

Calcium sulphate dissolves in insignificant amounts and when the temperature of the solution drops, it falls out of it and precipitates on the walls of equipment, pipes and gutters.

From an analysis of the behavior of the components of clinker in sulphate solutions, it is visible that sulphides and ferrites of metals do not dissolve in weakly acid solutions. This leads to a decrease in the extraction of metals in the solution. Increasing the concentration of sulfuric acid and the temperature of the leaching process leads to the formation of silicic acid (H₂SiO₄) and other side reactions, which complicates the further separation of the phases.

In this respect, the leaching of clinker in chloride solutions is of particular interest.



Hydrochloric acid is more expensive than sulfuric acid. However, it is possible to reduce the cost of the process if chloride solutions are obtained by electrolysis of sodium chloride and the leaching and electrolysis process is carried out simultaneously in the same unit.

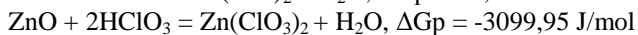
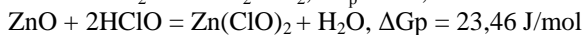
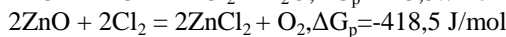
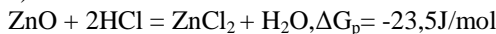
The ease of formation of many metal chlorides, their low boiling point, high volatility and solubility in water have long attracted the attention of chemists and metallurgists as factors favorable for processing ores of non-ferrous and rare metals. The use of elemental chlorine and various chlorine-containing substances has become firmly established in the modern practice of a wide variety of metallurgical and electrochemical processes.

According to the literature [6], the electrolyte composition in the process of electrolysis of alkali metal chloride solutions will vary not only depending on the conditions of electrolysis, but also depending on the composition of the electrolyte, which will determine the reactivity of the solvent.

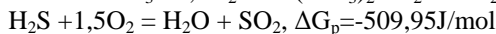
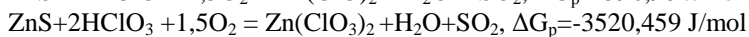
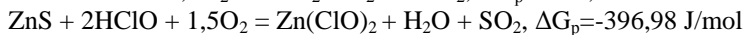
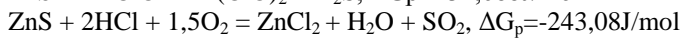
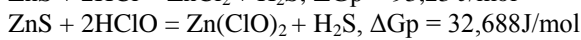
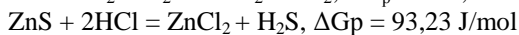
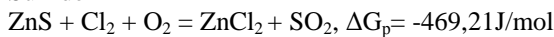
As it is known, the direction of the reaction can be judged by the value of the Gibbs energy of the reaction. Therefore, we calculated the Gibbs energy value of all possible reactions by the Vladimirov method [7].

When leaching clinker with this electrolyte with clinker components, the following reactions can occur

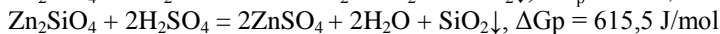
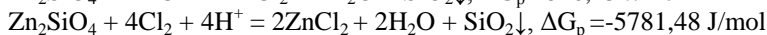
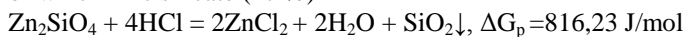
a) reactions with zinc



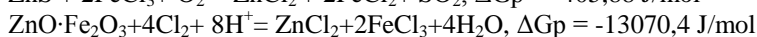
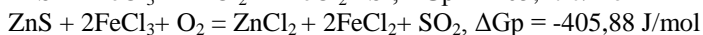
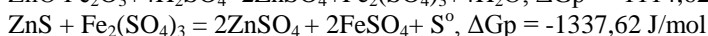
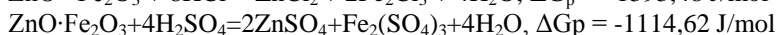
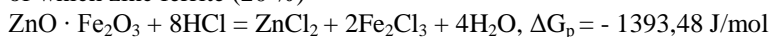
Sulfide



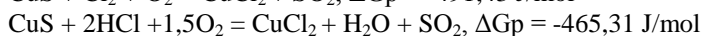
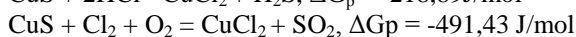
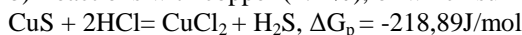
of which zinc silicate (17 %)



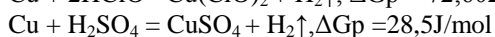
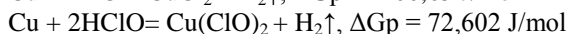
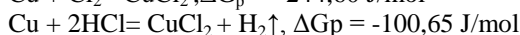
of which zinc ferrite (20 %)



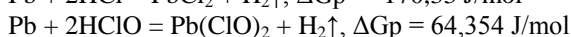
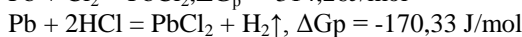
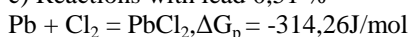
b) Reactions with copper (2.2 %), of which sulfide 70-80 %



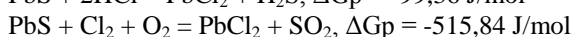
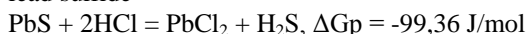
metal 20-30 %

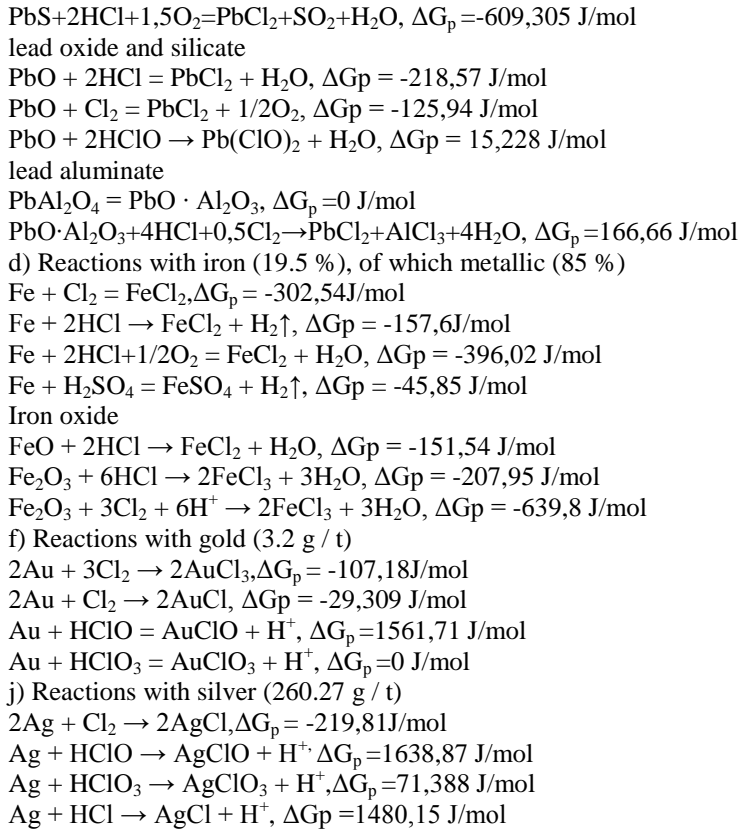


c) Reactions with lead 0,51 %



lead sulfide





The change of the value of Gibbs energy above the reactions shows that zinc and its compounds, as well as copper, lead, iron, gold and silver, all interact well with chlorine to form water-soluble compounds, hence their dissolution is possible. Noble metals do not interact with chlorine compounds.

VI. CONCLUSION AND FUTURE WORK

As a result of thermodynamic analysis, the following conclusions were made:

- sulfides and ferrites of metals in sulfuric solutions do not dissolve in weak acid solutions. It leads to a decrease in the extraction of metals in the solution. An increase in the concentration of sulfuric acid and the temperature of the leaching process leads to the formation of silicic acid (H_2SiO_4) and other side reactions, which complicates further phase separation;
- chloride solutions obtained by the electrolysis of sodium chloride are much cheaper than acids, during the process of leaching and electrolysis simultaneously in the same unit;
- thermodynamic analysis established that the main part of chlorine is consumed to dissolve iron. Therefore, prior to electroleaching, it is necessary to remove iron from the clinker;
- gold and silver are more electropositive elements than the others and their concentration is lower, therefore, they interact with chlorine as a last resort, and therefore may remain in the cake.

REFERENCES

- [1] Sanakulov K.S. Scientific and technical basis for the processing of mining and metallurgical wastes. Tashkent. Publishing House Fan ANRUz2009.404 p.
- [2] Panshin A.M. Complex processing of clinker by Electro-zinc. The materials of the symposium "Miner's Week 2008" MSTU 2009, 298-302 p.
- [3] The patent for the invention №2356960. The method of processing waste zinc production. November 15, 2006.
- [4] Klein S.E., Kozlov P.A., Naboichenko S.S. Extraction of zinc from ore raw materials. Yekaterinburg. UGGU-UPI 2009. 492 p.
- [5] Allabergenov R.D., Akhmedova R.K., Mikhailov S.V. "Zinc production clinker is a new polymetallic mineral raw material of non-ferrous metallurgy and ways of its complex processing". Uzbek chemical journal of the Academy of Sciences of the Republic of Uzbekistan. Tashkent 2012. №3.43-49 p.





ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 6, Issue 4, April 2019

- [6] Maksimov V.N. Electrochlorination as a method of complex metal extraction. M. Metallurgizdat, 1995, 206 p.
[7] Vladimirov L.P. Thermodynamic calculations of metallurgical reaction equilibrium. M.; Metallurgy. 1970. 528 p.
[8] Kholiqulov D.B., Samadov A.U., Boltaev O.N., Akhtamov F.E. The results of laboratory research processing of zinc cake zinc plant JSC "Almalyk MMC". European science review, Premier Publishing s.r.o. Vienna. 2018. #11-12. - Pp. 96-99.
[9] Abdurahmonov S.A., Akhmadzhonov U.M., Uurbonov Sh.K., Toshodirova R.E. Extraction of valuable components from zinc production wastes. Uzbekistan concupial habarnomasi. 2010. №2 (41) p. 83-86.
[10] Abdurahmonov S.A., Akhtamov F.E., Toshqodirova R.E. Electroleaching of zinc clinker production. "Uzbekistan konchilik havarnomasi" ilmiy-technician va and islab chishish magazine. 2014. №2 (57) p.82-84.

№	Full name place of work, position, academic degree and rank	Photo
1	Abduraxmonov Soib, professor of Department of Metallurgy, Tashkent state technical university Almalyk branch, Dr.Sci.Tech., professor	
2	Toshkodirova Rano Erkinovna, senior teacher Department of Metallurgy, Tashkent state technical university Almalyk branch	
3	Kholiqulov Doniyor Bakhtiyorovich, Deputy Director for Research and Innovation Almalyk branch of the Tashkent state technical university, PhD, associate professor	