Complex Processing of Industrial Products and Lead-Copper Concentrates

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Abstract

This article describes the modern technologies of processing of industrial products and copper-lead waste products, and their physical and chemical properties as well as laboratory tests for processing slurries and zinc slags. Experiments have shown that the temperature of the melt in the reduction of lead-containing slag should be within 1100–1200 °C. The key criteria for separating melting products to different phases are the difference in density, viscosity and surface tension of the melted slag. The separation of the molten slag to the phases and the reduction of the settling time of the melt in the furnace will be promoted by the increasing the density and surface tension of the lead and matte-molten slag, and reduction in viscosity of the latter. The processing of lead-copper-zinc containing sulfide raw material was carried by the reduction smelting method and the purging of melt with a natural gas at a rectangular electric furnace. Dust collection system was connected to the furnace through the duct work. The feedstock loading was carried out through the furnace crown. The purging of melt with natural gas was performed after the melting of the charge using the immersed gas supply tube. The gaseous products were derived from the melting furnace through the flue. The gas supply tube was fitted with a gear system to adjust the depth of the tube immersion. As results of experiments were obtained sharply separable intermediates with a high degree of concentration: lead into lead bullion to 92–94%; copper into matte to 90–91%; zinc to the slag and sublimates to 94–96%. Thus the material costs for processing of copper matte and zinc slag will be reduced and the yield of sublimates consisting primarily of vapor and metallic zinc sulfide will be decreased.

1. Introduction

Currently, industries pay a great attention to improving the efficiency of the integrated use of mineral resources, environmental issues and reduce the harmful emissions at the metallurgical enterprises. The direct reduction of polymetallic sulfide raw materials using natural gas is one of the most effective ways of processing. This method is suitable for processing lead concentrates and intermediates (copper slurry, slag and matte), and the copper-lead-zinc concentrates.

Currently, for the production of lead and copper are mainly used pyrometallurgical methods [1–4].

The existing scheme for processing lead raw materials i.e. sinter roasting and recycling of roaster gases (blast smelting – refining) provides 95% of world production of lead, but it cannot fully solve a wide range of problems of the lead industry. The growth of involving sulphide polymetallic sulphide ores and concentrates in metallurgical processing requires finding a way to direct production of lead, bypassing intermediate technological conversions.

Currently new processes of direct lead production are being implemented. They increase the complexity of the use of raw materials and other qualitative indicators of technology. Among these methods, autogenous smelting takes the main place. Advantages of the new process:

- Use of heat of sulfides oxidizer for heating;
- Melting of the charge and the compensation of heat losses;
- Full utilization of sulfur-containing gases and significant emissions reduction of harmful substances into the atmosphere;
- High specific productivity;
- The reduction or complete absence of fuel costs;
- Complex automation and mechanization of the process;
- A significant improvement of working conditions, etc.

The processes of applying autogenous smelting and other pyrometallurgical processes for lead production from sulphide concentrates are characterized by high technical and economic indicators. These processes are based on the use of high-performance and cost-effective units for improving the working conditions of staff. The choice of the process depends on the cost of electricity, liquid and gas fuels. Prospects of development of the lead industry are mainly associated with the use of oxygen injection without preliminary sintering, using cheap coal reducers and the high use of secondary energy resources.

A method for obtaining the sulphide lead concentrates or smelting without preliminary agglomeration is patented by Australian firms Mount ISA, Mines Ltd. and CSIRO (Commonwealth Scientific and Industrial Research Organization), UK Patent №2113253A.

The ore or concentrate as a powder or slurry is loaded into the furnace lined with refractory to melt during 1000–1250 °C. The stirring of the melt is carried out by oxygen-enriched air, which, like the liquid fuel is fed downward through submerged tuyeres. The first stage oxidizes lead sulphide PbS and is absorbed by slag containing 50% lead in the form of oxides. In the second step lumped coals are charged into the furnace for recovery of the metal oxide to metal. Slag either recycled or sent for further processing to extract zinc. The process can be conducted in a continuous mode [5].

“The single-stage process for producing lead from sulphide concentrates” refers to a species of new roast-reaction smelting processes of rich lead concentrates. The method is patented by St. Joseph Lead Co.

Dry concentrate, flux and air are supplied to the melt of lead concentrate through a lead bath. Oxygen-enriched air or fuel heated from 800 to 1050 °C. In the melt a major amount of lead oxidized to lead oxide is by atmospheric oxygen, which reacts with the injected sulphide concentrate and allocates metallic lead and sulfur dioxide.

The tests were conducted in a semi industrial scale through a converter at St. Joseph Co. Ice Company. Reduction of sulphide materials by hydrogen and natural gas is a new direction in the creation of effective technologies for the production of lead. This method exists for a long, and there is a tendency of its widespread use in reduction technology of heavy and non-ferrous metals [6].

American researchers [7] proposed to conduct sublimation of lead sulfide from rich concentrate (76.4% Pb) in a stream of inert gas (helium, argon) at 1000–1100 °C. After that the gas stream enters into the reduction zone of the furnace, which is also fed by hydrogen. Extraction of lead is 98%.

In recent years, a significant number of works devoted to the reduction of sulphide materials with natural gas. The authors of [8] analyzed the thermodynamic ability of reducing lead sulfide, iron and zinc by methane. Calculations have shown that the reduction reaction of lead sulfate proceeds easily, even at medium temperatures 700–900 °C. Reduction of iron and zinc sulphides requires higher temperatures – more than 1400 °C. Some questions of the kinetics of reduction of sulfides of lead, copper and zinc are listed in [9–10].

Currently, scientists are also investigating the processes of direct production of non-ferrous and rare metals from sulphide material.

2. Experimental

The article describes technology that allows intensifying the process of direct reduction and production of non-ferrous metals from sulfide raw material under a layer of zinc slag. Therefore preliminary experiments were conducted to study the viscosity and surface tension of slag and mixtures of slag with slurries. Tests of thermo-gravimetric installation with direct blowing of the melt were carried out. The experimental setup is shown in Fig. 1. The degree and rate of reduction of lead and zinc sulfides, depending on the temperature and duration of treatment were studied [11].

The sequence of experiments: raw material was placed in the reaction crucible (2); plates of capacitor (9) and a condenser (10) were placed in the cold zone of the reaction crucible; heating furnace (3,7) and the inlet of feed gas from cylinder to the gas inlet tube (5) to the desired temperature in the furnace.

The condenser with refrigerator was used mainly for trapping zinc sublimates which are fused at its plate 9. Recycled lead 85–87% remained in the reaction crucible.

The condensation measurement was carried out by strain gauge 13, measuring the mass of the condensate with automatic recording system at electric potentiometer 15. The exhaust gases are diverted to chromatograph through the pipe 16.

The degree of reduction of metal sulfides was determined according to X-ray and chemical analysis of the products of the reaction, a recovery rate by the amount of exhaust gases, condensed sublimates, and
the concentration of the monitored component in the exhaust gases.

The results of studies determining the degree of reduction of lead and zinc sulfides with hydrogen are shown at Table 1 and Fig. 2.

The table shows that the degree of lead reduction is much higher than the degree of zinc reduction, especially at a temperature of 900–1000 °C.

It is seen that the recovery rate of lead sulfide is much higher than the rate of zinc sulphide recovery, especially in the range 1100–1200 °C.

Table 1

<table>
<thead>
<tr>
<th>Treatment time, min</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>900</td>
</tr>
<tr>
<td>Lead sulfide</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>14.8</td>
</tr>
<tr>
<td>20</td>
<td>29.2</td>
</tr>
<tr>
<td>30</td>
<td>40.4</td>
</tr>
<tr>
<td>40</td>
<td>51.7</td>
</tr>
<tr>
<td>Zinc sulphide</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.8</td>
</tr>
<tr>
<td>20</td>
<td>4.7</td>
</tr>
<tr>
<td>30</td>
<td>8.4</td>
</tr>
<tr>
<td>40</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Fig. 2. Lead (1) and zinc (2) reduction rates depending on temperature.

The slag plays a crucial role in metallurgy. The chemical composition of the slag, their specific gravity, viscosity, surface tension and other physical and chemical properties influence the distribution of valuable components in the metallurgical smelting of polymetallic raw materials.

Any violation of the processing technology, its parameters, chemical and mineralogical composition of raw materials and fluxes leads to the loss of valuable components with basic slag, as well as to the deterioration of the conditions of separation of smelting products. Consequently, there is need for a detailed study of physical and chemical properties of lead production’s slags.

The tests of the two slags of lead plants (Table 2) were conducted. Slag I was produced in the smelting of lead concentrates with the issue of lead and matte; II slag produced from the smelting of lead concentrates to cupreous lead: slag III – during the concentration smelting of the poor matte, speiss, slurries and other recycles.

The speiss formed during smelting raw materials rich in arsenic and antimony and slurries obtained from the refining of lead, have a complicated structure comprising metallic lead, lead sulfide, various kinds of copper, arsenides of copper and iron and copper antimonide [12].

The converting speiss with mattes is the most common method of processing speiss. The method allows extracting to the converting copper for about 95% of copper, gold and silver.

The difference in the values of viscosity and density of the matte-slag melts is one of the main criteria determining the phase separation in the bath of furnace. Increasing the difference in densities of matte and molten slag, and particularly decrease in the viscosity of the last facilitates the separation of the phases, reduces settling time of the melt in the furnace and reduces the mechanical losses of metal matte with the slag.
The experiments determining the viscosity of the slags is a complex process related to the measurement in aggressive melts at high temperatures [13]. Probably why the definition of viscosity is still not standardized, and almost every study begins with the design of the viscometer.

There are many different viscometers with different operating principle, for example, viscometers with coaxial cylinders. In such cylinders the outer cylinder rotating and internal is stationary or inner cylinder immersed in the melt spinning and the outer cylinder remains stationary. Alignment is the main drawback of these viscometers. The slightest change in one of the cylinders relative to the axis causes large errors.

The project team developed an apparatus for measuring the viscosity shown in Fig. 3. This viscometer allows avoiding errors in measurement. Its operating principle: the body amplitude oscillating in the slag varies depending on the viscosity of the slag.

Table 2
Composition of slags, %

<table>
<thead>
<tr>
<th>Slags</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore smelting I</td>
<td>0.72</td>
<td>1.52</td>
<td>11.0</td>
<td>36.5</td>
<td>23.4</td>
<td>15.3</td>
<td>6.8</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>Ore smelting II</td>
<td>0.47</td>
<td>2.28</td>
<td>11.6</td>
<td>34.38</td>
<td>19.6</td>
<td>16.13</td>
<td>12.26</td>
<td>1.81</td>
<td>1.2</td>
</tr>
<tr>
<td>Concentration smelting III</td>
<td>1.07</td>
<td>1.14</td>
<td>6.2</td>
<td>41.2</td>
<td>19.6</td>
<td>16.3</td>
<td>12.26</td>
<td>1.81</td>
<td>1.2</td>
</tr>
<tr>
<td>Electric settler IV</td>
<td>1.02</td>
<td>4.06</td>
<td>17.32</td>
<td>42.7</td>
<td>17.3</td>
<td>5.8</td>
<td>3.65</td>
<td>2.1</td>
<td>2.3</td>
</tr>
</tbody>
</table>

If the body or the probe suspended elastically is placed in a viscous medium and occasionally act on it, then the probe will perform forced oscillations, the oscillation amplitude is inversely proportional to the viscosity of the slag.

\[ \eta = \frac{A}{\frac{1}{\rho} \sigma^2} \]  

where in \( A \) – a constant that is determined experimentally by a fluid with known viscosity; \( \rho \) – density of the liquid; \( \sigma \) – oscillation amplitude of probe dropped into the melt.

The electronic vibrating viscometer determining the viscosity eliminates errors caused by deviation of the probe from the axis of the crucible and accurately determines the depth of immersion of the probe into the melt.

The main criteria for determining the phase separation in the bath furnace is the difference in the values of viscosity and density of the molten slag. Experimental setup for determining the viscosity by electronic vibrating viscometer is shown in Fig. 3. A slag sample is heated in an electric furnace (1). The temperature in the furnace is measured by platinum-platinum-rhodium thermocouple (4) and recorded with the potentiometer (5). The sample in the crucible (3) is placed in a glass reactor (2). Adjusting the heating of furnace is carried out by a transformer.

The immersion depth of the probe in the matte-slag melt is controlled by a special holder (6). The electronic vibrating viscometer consists of: a measuring unit (7), the probe (8), the unit of excitation and amplification information signals (9), reporting changes in the amplitude of vibration of the probe, which are converted to millivolts and recorded by millivoltmeter (10), flask (11) with sulfuric acid and calcium chloride for drying the gases; an autotransformer (12) to adjust the current in the furnace.

Research on processing of lead production slags and the study of their viscosity as a function of the main technological parameters [14] were carried out at the industrial slag produced after the basic metallurgical processes and taking into account the above facts.
The viscosity studying experiments were conducted: on a slag (1) obtained after smelting the slurries; on a slag (2) obtained after the joint melting of slurries and lead concentrates with blowing natural gas; and on a slag (3) obtained by venting lead concentrate with natural gas. The compositions of initial materials are shown in Table 3.

Table 3

<table>
<thead>
<tr>
<th>Slag</th>
<th>Pb</th>
<th>ZnO</th>
<th>Cu</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>FeO</th>
<th>FeS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.8</td>
<td>2.14</td>
<td>1.4</td>
<td>22.9</td>
<td>26.4</td>
<td>10.6</td>
<td>-</td>
<td>33.5</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1.1</td>
<td>2.26</td>
<td>0.4</td>
<td>23.7</td>
<td>28.2</td>
<td>12.1</td>
<td>-</td>
<td>30.0</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>0.7</td>
<td>0.81</td>
<td>0.21</td>
<td>15.7</td>
<td>36.5</td>
<td>16.2</td>
<td>-</td>
<td>29.8</td>
<td>-</td>
</tr>
</tbody>
</table>

The analysis of the measurements shows that at lower temperature from 1000 °C to 750 °C viscosity of lead production slags increased marginally i.e. 2 to 4, with \( n \times s/m^2 \). A further decrease of temperature leads to a sharp increase in viscosity. Optimum viscosity is achieved at a processing temperature of 1000–1200 °C due to the decreasing of lead and copper losses.

In Fig. 4 shows the dependence of the viscosity logarithm to inverse of the absolute temperature, described by straight lines. The activation energy of viscous flow \( E \) is the energy required for the transition of particles from one equilibrium position to another.

The position is determined by the linear temperature dependence of viscosity in semi-logarithmic coordinates. The activation energy of the viscous flow for the slag (2) is equal to 2.5 kJ/mol, and for the slag (3) – 22.6 kJ/mol, in the range 800–1000 °C [15].

The study of surface tension and density of the slag from the temperature are shown in Fig. 5. The experiments were conducted on the slag (2) and slag (3) obtained after purging the lead concentrate with natural gas (Table 2).

Figure 5 shows that the surface tension of lead production’s slag is largely dependent on the temperature. Since an increase in temperature from 700 to 820 °C decreases the surface tension of the slag on \( 1.5-1.8 \times 10^{-2} \) J/m², respectively, to slag (2) and slag (3). It was established that to reduce the loss of metal with lead production’s slag the temperature of the melt should be kept within 1100–1200 °C.

The obtained experimental data on the viscosity, surface tension and density of the slag in the tested temperature range is in good agreement with those authors studies [12–13].

3. Results and Discussion

The existing technological schemes of processing of raw materials in the production of lead relates to the clean selective monometallic concentrates. Currently, productions are increasingly using complicated polymetallic raw materials, particularly collective concentrates and intermediate products.

An acute problem of lead production is the selective separation and fuller recovery in commodity products such metals as copper and zinc. Their
extraction to copper matte and zinc sublimates does not exceed 80–85%. The technology of direct reduction of sulfides of heavy non-ferrous metals with natural gas was developed by a group of scientists of KazNTU n.a. K.I. Satpaevyev. It allows to selectively divide lead, copper and zinc in separate products suitable for further processing.

The results showed that the process of direct reduction of lead-sulphide concentrate during gas feeding to the surface of the material has the following disadvantages. The allocation of lead between the recovery products is unsatisfactory and sublimates are essentially collective product consisting of lead and zinc sulfide.

The melting of the charge for the transfer lead into crude metal is recommended to carry out under a layer of metallurgical slag.

Theoretical studies and data [16] showed that the processes of recovery of lead and zinc sulfides under the slag layer proceeds by the following reactions:

$$2\text{PbS} + \text{CH}_4 = 2\text{Pb} + \text{C} + 2\text{H}_2\text{S}$$

$$2\text{ZnS} + \text{CH}_4 = 2\text{Zn} + \text{C} + 2\text{H}_2\text{S}$$

$$4\text{PbS} + \text{CH}_4 = 4\text{Pb} + \text{CS}_2 + 2\text{H}_2\text{S}$$

$$4\text{ZnS} + \text{CH}_4 = 4\text{Zn} + \text{CS}_2 + 2\text{H}_2\text{S}$$

$$2\text{CuFeS}_2 \rightarrow \text{Cu}_2\text{S} + 2\text{FeS} + 1/2\text{S}_2$$

$$2\text{Cu}_2\text{S} + \text{CH}_4 = 4\text{Cu} + \text{C} + 2\text{H}_2\text{S}$$

The oxides of iron and zinc in the composition of slag also react with methane:

$$\text{CH}_4 + 3\text{FeO} = 3\text{Fe} + 2\text{H}_2\text{O} + \text{CO}$$

$$\text{CH}_4 + 4\text{FeO} = 4\text{Fe} + 2\text{H}_2\text{O} + \text{CO}_2$$

$$\text{CH}_4 + 3\text{ZnO} = 3\text{Zn} + 2\text{H}_2\text{O} + \text{CO}$$

$$\text{CH}_4 + 4\text{ZnO} = 4\text{Zn} + 2\text{H}_2\text{O} + \text{CO}_2$$

Unreacted methane and hydrocarbons are pyrolyzed:

$$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$$

$$\text{C}_n\text{H}_m \rightarrow n\text{C} + m/2\text{H}_2$$

and further

$$\text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO}_2$$

$$\text{ZnO} + \text{C} \rightarrow 2\text{Zn} + \text{CO}_2$$

$$\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$$

$$\text{ZnO} + \text{CO} \rightarrow \text{Zn} + \text{CO}_2$$

$$\text{FeO} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2\text{O}$$

$$\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}$$

$$\text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O}$$

$$\text{ZnO} + \text{H}_2 \rightarrow \text{Zn} + \text{H}_2\text{O}$$

Metallic iron, copper and partially zinc react with lead sulfide and reduce it to metal by the following reactions:

$$\text{PbS} + \text{Fe} = \text{Pb} + \text{FeS}$$

$$\text{PbS} + \text{Zn} = \text{Pb} + \text{ZnS}$$

$$\text{PbS} + 2\text{Cu} = \text{Pb} + \text{Cu}_2\text{S}$$

The addition of limestone to the charge in the form of CaO during melting

$$\text{ZnS} + 1.5 \text{O}_2 + \text{CaO} \rightarrow \text{ZnOCaO} + \text{SO}_2$$

$$\text{FeS} + 1.5 \text{O}_2 + \text{CaO} \rightarrow \text{FeOCaO} + \text{SO}_2$$

leads to the appearance of the final products of the process: metal lead and matte, where iron is concentrated, copper, zinc containing slag, partially sublimates and low toxic gases consisting mainly of water vapor, nitrogen, carbon dioxide and sulfur dioxide.

Theoretical, experimental and laboratory studies allowed to carry out tests on processing of lead-zinc-copper-sulfide raw materials by the reduction smelting method and the purging of melt with a natural gas. Dust collection system consisting of a cyclone and a filter to trap fine dust was connected to the furnace through the duct work. The feedstock loading was carried out through the furnace crown. The purging of melt with natural gas was performed after the melting of the charge using the immersed gas supply tube.

The gaseous products were derived from the melting furnace through the flue. The gas supply tube was fitted with a gear system to adjust the depth of the tube immersion. Initially a series of experiments was carried out with a charge consisting of lead concentrates, slurries and zinc slag [17]. The composition of the processed feedstock: 25% slurries, 50% lead concentrate and 25% of granulated slag (Table 4).

The collective copper-lead-zinc concentrate containing, %: Cu – 18.2; Pb – 22.4; Zn – 5.2; Fe – 15.6; S – 26.3 also was subjected to direct reductive processing. The temperature in the furnace was 1200–1250 °C.
The sequence of operations: the melt of copper-lead-zinc concentrates under a layer of zinc slag was added to the initial charge consisting of lead concentrate, slurries and the slag. The calcium oxide in a ratio of 1.2–1.3:1 was added according to the content of zinc at the source sulfide material. The entire melt was purged with a natural gas for 45–50 min until the formation of a lead bullion, matte and slag. In the second stage, the resulting slag and matte was purged with air and natural gas for 25–30 min consecutively. The results of experiments are shown in Table 5.

The sharply separable intermediates with a high degree of concentration of lead in the lead bullion to 92–94%, copper into matte up to 90–91%, and of zinc in slag and fumes at 94–96% were obtained.

4. Conclusion

Processing of a melt of lead concentrates and intermediates (matte, slurries, speiss, and dust) using natural gas as a reducing agent leads to the formation of four independent products: lead bullion, copper matte, slag and zinc sublimes. The composition of the slag and its physical and chemical properties greatly affect the distribution of the valuable components.

The physico-chemical study of lead slag was carried out. It was established that the temperature of the lead-containing slag must be maintained within 1100–1200 °C in order to reduce losses of metal with slag. The difference in density, viscosity and surface tension of the melted slag is one of the main criteria for determining the phase separation in the bath of the furnace.

The optimum value of slags viscosity allowing to minimize the loss of non-ferrous metals with the slag was established. On the basis of theoretical and experimental studies there were carried out tests on the processing of lead-zinc-copper sulfide raw materials by reduction smelting and purging of melt with a natural gas.

The tests resulted in obtaining sharply separable intermediates with a high degree of concentration to individual commodity products: Lead to lead bullion up to 92–94%; copper to matte up to 90–91%, zinc to slag and fumes up to 94–96%.

This method can significantly reduce material costs and energy costs in the further processing of copper matte, zinc slag and decrease the output of the sublimates consisting mainly of sulfide and metallic zinc vapors.

The developed technology of direct reduction of sulfides of heavy non-ferrous metals with natural gas allows to selectively divide lead, copper and zinc in separate products suitable for further processing.

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