Technological experiments of joint smelting of lead intermediate products, recycled materials and high-sulfur copper-zinc concentrate

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Abstract. The purpose of this work is to improve the technological indicators of the existing mine contractile smelting technology by joint smelting of intermediate products, recycled materials of lead production with high-sulfur copper-zinc concentrate. It is established that during the smelting of copper-zinc concentrate which is difficult to process, high selective extraction of copper into matte and zinc into slag is achieved in one stage. The method consisted in the joint smelting of lead intermediates and high-sulfur copper-zinc concentrate in an electric furnace at a temperature of 1250 °C under conditions of sequential blowing of the melt with air, then with natural gas. It is established that when the melt is purged with air and natural gas for 20 minutes, an equilibrium distribution of metals between the melting products is achieved. It is shown that simultaneous use of copper-zinc concentrate as a sulfidizer reduces the content of copper and lead in slag, increases the extraction of arsenic and antimony into the dust. Consumption of coke and quartz flux is reduced in comparison with the existing technology from 6.7 to 2.5% and from 12.5 to 2.8% of the initial feed weight, respectively, which significantly reduces material and energy costs of the process. As a result of extensive laboratory testing, the optimum composition of the new charge has been selected. Metal distribution between smelting products of the new charge with addition of 30% of high-sulfur copper-zinc concentrate was established. High recovery of copper to the matte up to 94.8%, against 83.7% according to the existing technology; lead to the rough lead - up to 93.6%, against 70.8%; zinc to the slag - up to 94.7%, against 83.7%; arsenic to the dust - up to 91%, against 69.5% and antimony to the dust - up to 92.3%, against 60.0% according to the existing technology. Keywords: charge, intermediate product, recycled materials, copper-zinc concentrate, distribution, recovery, coke, slag, matte, metal.

Introduction

When processing substandard intermediate products and recycled materials, none of the existing lead production processes achieves high recovery of valuable metals. There is not enough deep sublimation of arsenic and antimony into dust, which reduces their removal from the main production [1, 2]. Their accumulation is growing in the main production, which increases material and energy costs of lead and copper production. The use of known barbotage autogenous processes (Q-S-L, Isasmelt, “Vanyukov Process”, etc.) for the solution of the listed actual problems is restrained by a set of reasons: high volatility of lead compounds; insufficient calorific value of processed materials;
complexity of composition of initial charge from which it is necessary to extract the maximum of valuable components [3, 4, 5]; necessity of using of expensive coke; complexity of equipment design, etc. [5, 6].

The existing technology of processing of substandard intermediate products and recycled materials at KazZinc Ltd. is based on mine contractile smelting. The process is characterized by high consumption of expensive coke and significant emissions of low by SO2 hard-to-recover gases into the atmosphere. The technology is designed for processing of a complex conglomerate of a mixture consisting of copper-lead matte from mine blast smelting, converter slag and recycled materials from refining of rough lead: copper slips, alkaline melts, lead cokes, etc. Compositions of substandard sulphide intermediate products are not stable and vary widely. For example, lead-copper mattes contain, %: Cu - 10-20, Pb - 12-25, Zn - 8-12, As – up to 1.5, Sb – up to 1.0; copper slips, %: Cu - 15-20, Pb - 18-30, Zn - 2-4, As – 4.0, Sb - up to 2.5. From recycled materials the converter slag attracts attention, % (wt.): Cu - 3-5, Pb - up to 34, Zn - up to 4.5, As - 2-2.5, Sb - up to 2.0, which is the main part (up to 30%) in the structure of the initial charge of mine contractile smelting.

During the smelting of the initial charge, significant volumes of non-ferrous, precious, rare and rare-earth metals as well as associated hazardous metal impurities (As, Sb) circulate in the technological chain "smelting-converting". As a result, valuable metals are distributed in the smelting products, and the accompanying impurity metals (As, Sb) accumulate in the technological chain, which reduces the quality of the obtained products, increases the negative impact on the environment and life safety of workers. The objective of the technology is recovery of base metals - copper and lead. However, extraction of copper to the matte is low, around ~ 83%. Extraction of lead to the rough lead hardly reaches the level of 70%. The low lead recovery is due to its high content in matte (up to 25%), which is the main part (up to 30%) in the structure of the initial charge of mine contractile smelting.

It is relevant to take more promising decision on processing the obtained lead intermediate products and recycled materials with copper-zinc concentrate. This decision is supported by the production of high sulphur copper and zinc concentrate at the Nikolayev deposit in the East Kazakhstan region.

Copper-zinc concentrates in copper production are traditionally considered to be “technologically inconvenient” and as raw materials difficult to process primarily due to the presence in tangible (significant) concentrations of zinc and lead at considerable copper content (18-20%). For complex processing of lead intermediate products and recycled materials polymetallic sulphide copper-zinc concentrate is the most suitable (optimal, unique) material (feed charge component, natural reagent), performing the role of "former" of the main condensed smelting products - lead, matte and slag. The concentrate contains all the necessary components (elements): lead, copper, zinc and sulfur, available amount of each can be used in order to effectively separate lead, copper and zinc from recycled materials to obtain high quality products - rough lead bullion, copper matte and zinc slag.
Direct processing of high-sulfur copper-zinc concentrate with its simultaneous use as a sulfide reagent in the process of smelting would allow in one stage to recover as much lead into the rough metal, copper to the matte, zinc to the slag from the processed materials, including the concentrate. This way of improving the processing of lead intermediate products and recycled materials from the point of view of practice looks attractive due to the development of mine contractile smelting, accumulated experience of its operation and minimum capital costs during industrial implementation.

The purpose of the present work is to define the main technological parameters of the technology of joint smelting of intermediate products, recycled materials of lead production with high sulfur copper-zinc concentrate under conditions of enlarged laboratory tests.

Table 1 – Chemical composition of intermediate products, recycled materials and flux of the lead production

<table>
<thead>
<tr>
<th>Name of material</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Fe</th>
<th>S</th>
<th>As</th>
<th>Sb</th>
<th>SiO₂</th>
<th>CaO</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper slips</td>
<td>29.0</td>
<td>36.0</td>
<td>4.0</td>
<td>8.77</td>
<td>3.87</td>
<td>1.4</td>
<td>0.56</td>
<td>–</td>
<td>–</td>
<td>16.96</td>
</tr>
<tr>
<td>Low by main metals matte of mine contractile smelting</td>
<td>20.85</td>
<td>19.5</td>
<td>11.4</td>
<td>16.7</td>
<td>11.1</td>
<td>1.1</td>
<td>0.56</td>
<td>–</td>
<td>–</td>
<td>18.79</td>
</tr>
<tr>
<td>Converter slag</td>
<td>3.83</td>
<td>33.5</td>
<td>4.54</td>
<td>15</td>
<td>–</td>
<td>2.3</td>
<td>0.94</td>
<td>21.66</td>
<td>5.4</td>
<td>12.83</td>
</tr>
<tr>
<td>Alkaline melts</td>
<td>0.08</td>
<td>61.7</td>
<td>24.1</td>
<td>–</td>
<td>–</td>
<td>0.97</td>
<td>1.4</td>
<td>–</td>
<td>–</td>
<td>11.75</td>
</tr>
<tr>
<td>Quartz Flux</td>
<td>0.62</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

With addition of the concentrate to the charge, the structure of the charge was adjusted with consideration of changes in the consumption of quartz flux depending on the amount of the added concentrate. Thus quantitative ratios of products (Table 1) in the initial charge remained at the level of industrial practice. The new composition of the initial charge consisted of a mixture: copper slips - 27.8%; charges of contractile smelting (CS), including low by copper-lead matte and oxidized recycled materials - 18.5%; converter slag - 24.0%; quartz ore - 4.7%; coke - 2.5% and copper-zinc concentrate - 22.5%.

The experiments were carried out at the temperature of 1250°C in an electric furnace of 100 kW with 100 mm in diameter electrode. The furnace size: width - 250 mm, length - 410 mm, height - 440 mm.

Weight of the initial charge sample ~ 2.0 kg. The method of conducting the experiments was as follows. The initial charge was loaded on pre-melted slag, and once smelted with the help of oxygen tubes, sequential blowing with oxygen (20 min.), then - with natural gas (20 min.) was carried out. The air and natural gas consumption was constant at 10 l/h. The duration of smelting was 40 minutes. Once blowing is done the melt settled for 20 minutes, and through the special boreholes, slag, matte and rough lead were released. Each experiment was repeated three times for reproducibility. There was a good convergence of results. The obtained samples of slag and matte were subjected to elemental analysis and mineralogical studies.

Elemental analysis of slag and matte samples was determined by Agilent 7700 Series ICP-MS (USA) inductively coupled plasma mass spectrometer. Microscope Neofot (Carl Zeiss AG, Germany) was used for mineralogical analysis of polished surfaces of solid slag and matte samples.

Results and discussion

The thermodynamic laws of physico-chemical processes occurring during the joint smelting of intermediate products, recycled materials, and high-sulfur copper-zinc concentrate were studied in our work [9, 10]. Taking into account the theoretical fundamentals already stated, the results obtained in...
this work are discussed from the point of view of general positions, which is the main interest for practice.

A comparative analysis of the results of the material flows balance of the existing technology and smelting of a new composition of the charge with copper-zinc concentrate is presented in Fig. 1. High technological performance was achieved by smelting a new composition charge. Rough lead output increases from 19.4 to 24%, and matte increases from 28.3 to 32%. The established decrease in dust yield (from 5.6 to 4.2%) is explained by the minimum of dust extraction during electric smelting and the deeper sublimation of arsenic and antimony into dust due to the use of high-sulfur copper-zinc concentrate.

![Material Flow Balance Diagrams](image)

**A)** – existing smelting technology; **B)** – charge smelting with addition of Cu-Zn concentrate.

**Figure 1** Comparative material flow balance

More than two-times decrease in quartz flux mass during the smelting of the initial charge with copper-zinc concentrate is clearly seen. It was established in [8] that an excess amount of quartz present in slags from industrial practice, not participating in the formation of slag (fayalite), is ~ 40% of its total amount in slag. This leads to a large yield of slag, which requires an increased consumption of coke (6.7% of the weight of the charge), which is additionally consumed to heat the slag and maintain the temperature in the furnace. As a result, the overall material and energy costs of the process increase. In addition, a large excess of free quartz increases the cost of the subsequent fuming process, where the slag is sent to extract zinc.

The material balance, compiled according to the results of elemental analysis of the compositions of the smelting products, is given in Table 2.

Based on the results of the material balance, the heat balance of the technology was calculated using a new composition charge with the addition of high-sulfur copper-zinc concentrate (Fig. 2).
A) – smelting of charge of existing technology;  
B) – smelting of new composition charge with the addition of high-sulfur copper-zinc concentrate.

**Figure 2** Heat balances of smelting of different charge (%)

**Table 2** Material balance of the joint smelting of a new charge composed of lead intermediate products, recycled materials and high-sulfur copper-zinc concentrate in an electric furnace at a temperature of 1250 °C

<table>
<thead>
<tr>
<th>Material</th>
<th>Total</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Fe</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Uploaded:</strong></td>
<td>kg</td>
<td>%</td>
<td>kg</td>
<td>%</td>
<td>kg</td>
<td>%</td>
</tr>
<tr>
<td>Charge</td>
<td>1997.1</td>
<td>100.0</td>
<td>312.2</td>
<td>100.0</td>
<td>451.7</td>
<td>100.0</td>
</tr>
<tr>
<td>Coke</td>
<td>47.1</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>1997.1</td>
<td>100.0</td>
<td>312.2</td>
<td>100.0</td>
<td>451.7</td>
<td>100.0</td>
</tr>
</tbody>
</table>

**Materials:**
- Rough lead
- Matte
- Slag
- Dust, gases
- Discrepancy

**Notes:**
- 40.9 kg 21.1 16.5 3.9 5.5 40.1 95.3 91.2
- 57.2 28.6 282.0 49.3 93.1 28.0 4.9 6.4 7.2 1.3 3.0 95.4 16.7 43.3 3.4 0.6 9.7
- 76.8 35.8 2.8 0.4 0.9 5.4 0.7 1.2 134.1 17.5 93.7 123.1 16.0 56.0 0.2 0.0 0.7
- 182.5 9.1 1.6 0.9 0.5 5.4 3.0 1.2 1.8 1.0 1.2 1.6 0.9 0.7 31.4 17.2 89.6
- 53.4 2.7 9.4 3.0 11.7 2.6 3.8 2.6 5.9 2.6 0.6 1.7
- 1997.1 100.0 312.2 100.0 451.7 100.0 146.9 100.0 226.0 100.0 35.6 100.0
It is easy to notice that a significant part of the heat deficit of the existing technology is covered by oxidation reactions of excess sulfur and high-sulfur compounds supplied with high-sulfur copper-zinc concentrate when smelting a new composition charge. At the same time, in comparison with the existing technology, coke consumption is decreased more than two times (Fig. 1). The distribution of copper, lead, zinc, arsenic and antimony between the products of smelting of a new charge with the results of smelting of the charge of existing technology, are given in Table 3, which shows significant changes in the distribution of metals in the direction of improvement.

### Table 3 Distribution of metals between smelting products of a new charge with the addition of high-sulfur copper-zinc concentrate

<table>
<thead>
<tr>
<th>Product name</th>
<th>Distribution*, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Rough Lead</td>
<td>8.5</td>
</tr>
<tr>
<td>Matte</td>
<td>88.9</td>
</tr>
<tr>
<td>Slag</td>
<td>1.6</td>
</tr>
<tr>
<td>Dust</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* numerator - existing technology; denominator - enlarged laboratory data.

Estimated recovery values of non-ferrous metals, arsenic and antimony to the targeted products have shown significant growth compared to the existing technology. Recovery of copper to matte increased from 88.9 to 94.8%; lead to rough lead from 70.8 to 93.6%; zinc to slag from 83.7 to 94.7%; arsenic to dust from 69.5 to 91%; antimony to dust from 60.0 to 92.3%.

Based on the results of enlarged-laboratory tests the preferred technological parameters of the technology of joint smelting of intermediate products, recycled materials and copper-zinc concentrate in the electric furnace at the temperature of 1250°C under reducing conditions were determined:

- Charge composition:
  - copper slips – 27.8%;
  - charge of contractile smelting – 18.5%;
  - converter slag – 24.0%;
  - quartz flux – 4.7%;
  - copper-zinc concentrate – 22.5%;
  - coke – 2.5%.

- Duration of sequential melt blowing:
  - by air – 20 min., by natural gas – 20 min.

- Settling time after blowing – 20 min.

- Slag composition, wt. %:
  - Cu – 0.4;
  - Pb – 0.7;
  - Zn – 17.5;
  - FeO – 20.7;
  - SiO₂ – 28.3;
  - CaO – 10.1.

- Recovery of metals into the targeted products:
  - lead to the rough lead – 92.0%;
  - copper to matte – 96.0%;
  - arsenic, antimony to dust – 91 and 89%, respectively.

Specification of technological parameters of complex technology of processing of lead intermediate products and recycled materials with high-sulfur copper-zinc concentrate requires further large-scale (with a large amount of initial charge) tests in a continuous mode.

### Conclusions

1 Mine contractile smelting in its existing intermediate products and recycled materials processing purpose cannot be considered as a prospect due to the low copper and lead recovery, low quality matte, rough lead and slag. Further processing of copper matte with high content of lead (~25%),
arsenic and antimony (in total up to 1.5 %) and zinc- containing slags is characterized by the use of risky, ecologically "dirty" converting and fuming processes, respectively.

2 The smelting of the new composition initial charge, consisting of intermediate products, recycled materials of lead production and optimal consumption of high-sulfur copper-zinc concentrate, in the electric furnace is the most preferable. This will simplify the process and significantly improve the quality of the obtained products by deep sublimation of arsenic and antimony into dust, as well as reducing lead losses in matte.

3 Adjustment of slag composition by addition of high-sulfur copper-zinc concentrate will allow to obtaining optimal composition of fusible zinc-containing slag Cu₂O-PbO-ZnO-FeO-CaO-SiO₂: ZnO=20-22%; FeO/SiO₂=0.8-0.9%; CaO=8-10%. The maximum solubility of ZnO and minimum concentrations of copper and lead in slag will be provided. The most effective way of further processing of such zinc-containing slags should be not by fumigation, but by a highly efficient Vanyukov barbotage process. As the results of preliminary calculations have shown, the use of two-zones Vanyukov furnace will allow processing not only current zinc-containing slags, but also accumulated copper, lead, zinc-containing dumped slags.

4 The results of enlarged-laboratory tests of smelting of new composition charge in electric furnace showed that it is not possible to get commercial copper matte in one stage (lead content in matte remains high enough - up to 12 %). In our opinion, the most promising way is organization of additional finishing of copper-lead matte in a separate unit before the converting.

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Құрғасынды жарылығы еңімдер мен айналықты материялдарды мыс-мырыш концентраттарымен бірге балқыту

Досмухамедов Н.К., Жолдасбай Е. Е., Құрмансейтов М. Б., Аргын А. А., Желдібай М. А.
Технологические опыты совместной плавки свинцовых полуфабрикатов, оборотных материалов и высокосернистого медно-цинкового концентрата

Досмухамедов Н.К., Жолдасбай Е.Е., Курмансейтов М.Б., Артын А.А., Желдабай М.А.

Аннотация. Цель настоящей работы – совершенствование технологических показателей существующей технологии шахтной сократительной плавки путем совместной плавки полуфабрикатов, оборотных материалов свинцового производства с высокосернистым медно-цинковым концентратом. Установлено, что при плавке трудно перерабатываемых медно-цинковых концентратах обеспечивается высокое селективное извлечение из них меди в штейн и цинка в шлак в одну стадию. Методика испытаний заключалась в совместной плавке свинцовых полуфабрикатов и высокосернистого медно-цинкового концентрата в электропечи при температуре 1250 °С в условиях последовательной продукции расплава воздухом, затем – природным газом. Установлено, что при продувке расплава воздухом и природным газом в течение 20 минут достигается равновесное распределение металлов между продуктами плавки. Показано, что одновременное использование медно-цинкового концентрата в качестве сульфидизатора снижает содержание меди в штейне, а цинка в шлаке, повышает извлечение мышьяка и сурьмы в пыль. Уменьшается расход кокса и кварцевого флюса по сравнению с существующей технологией с 6,7 до 2,5 % и с 12,5 до 2,8 % от веса шихты, соответственно, что значительно снижает материальные и энергозатраты на процесс. В результате укрупненных-лабораторных испытаний выбран оптимальный состав новой шихты. Установлено распределение металлов между продуктами плавки новой шихты с добавлением 30% высокосернистого медно-цинкового концентрата. Достигнуто высокое извлечение меди в штейне до 94,8 %, против 83,7 % по существующей технологии; цинка в черновой свинц – до 93,6 %, против с 70,8 %; цинка в шлак – до 94,7 %, против с 83,7 %; мышьяка в пыль – до 91 %, против с 69,5 % и сурьмы в пыль – до 92,3 %, против с 60,0 % по существующей технологии. Ключевые слова: шихта, полуфабрикат, оборотные материалы, медно-цинковый концентрат, распределение, извлечение, шлак, штейн, черновой свинец.

Литература

References


