Processing of polymetallic concentrate from waste recycling plants by distillation in vacuum

S A Trebukhov¹, V N Volodin¹, O V Ulanova², N M Burabaeva¹
and F Kh Tuleutay¹

¹Satbayev University, The Institute of Metallurgy and Ore Beneficiation JSC 29/133, Shevchenko Str., Almaty city, 050010, the Republic of Kazakhstan
²«DHZ» AG, 8154, Obergell, Breitlosstrasse, 10, Swiss Confederation

E-mail: vohubert@mail.ru

Abstract. The sequence of operations for the processing of secondary raw materials has been proposed based on the analysis of the physicochemical properties of the main metals: copper, zinc, lead and tin contained in the metal concentrate from waste processing, including the developing complete state diagrams of binary systems of copper with lead and zinc, including the melt-vapor phase transition in vacuum. The proposed technology includes preliminary smelting of the concentrate into roughing brass for composition averaging and subsequent distillative extraction of lead and zinc each into roughing metals at a temperature of more than 1000°C with a decrease in pressure from atmospheric to 30 Pa. Copper-base still bottoms can be processed in copper production. Technological studies have confirmed the fundamental possibility of such technological scheme.

1. Introduction
The problems of solid household waste lead to the improvement of technologies for their processing [1]. One of these is incineration resulting in slag formation with concentration of ferrous (up to 8%) and non-ferrous (2-3%) metals [2]. The current technologies make it possible to separate slags into concentrates of ferrous and non-ferrous metals [3]. The Swiss company DHZ AG, engaged in slag processing [4], receives several hundred tons of granulated metal concentrate, which is sold as copper scrap, containing 20-40% copper, 40-50% brass and 20-30% zinc. Brass can contain up to 5% tin and up to 10% lead. One of the expedient operations in the technological scheme of processing such raw materials can be the distillative extraction of zinc and lead into a separate product.

Comparative analysis of physical properties, in particular, boiling points and vapor pressures of volatile lead and zinc with low volatile copper and tin [5], does not imply the transition of the latter to the vapor phase during distillation due to the large difference in these values.

At the same time, the distillation separation of volatile metals from non-volatile ones is accompanied by a change in their concentration in the melt in a wide range, which is due to the transition of some metals to the vapor phase and the accumulation of the second in the still bottoms. In addition, a decrease in pressure is accompanied by a shift in the boundaries of the liquid-vapor phase transition in temperature by hundreds of degrees, which can lead to crystallization processes in the melt.

Moreover, if the considered systems lead – tin [6] and zinc – tin are fusible with relatively low temperatures of the liquidus line and the process of the appearance of crystals is unlikely, then for...
systems of copper with lead and zinc the process of solid phase formation takes place, and in the Cu – Zn system it is possible to shift the boiling point to the region of solid solutions. In this context the choice of technological conditions for the distillation process – temperature and pressure – is important.

2. Selection of technological conditions for the distillation process

The most complete information on the behavior of metals during heating in vacuum can be obtained from liquid – vapor phase transitions, the boundaries of which: boiling points and vapor composition allow determining the conditions of the technological process. Due to the fact that the evaporation of zinc and lead from melts is performed, as a rule, at 1 – 100 Pa, we have developed complete phase diagrams, including the vapor phase, of the copper – lead and copper – zinc systems for the indicated pressures.

When calculating the boundaries of liquid - vapor phase transitions, the boiling point was taken as the temperature at which the sum of the partial pressures of copper and lead or copper and zinc is equal to 1 or 100 Pa, and the composition of the vapor phase as a fraction of the partial pressure of the metal in the total pressure. The change in the temperature of the phase transitions of the condensed phase, which according to our calculations is less than 5.6·10⁻⁸°C, was not taken into account when developing the diagram. The metals vapor pressure was borrowed from [7] paper in the copper-zinc system, and from [8] paper in the copper-lead system. The boundaries of the fields of liquid and vapor coexistence (L + V) at 100 and 1 Pa (the latter are shaded) are plotted on the state diagrams from the reference publication [9] (figures 1 and 2).

On the Cu – Pb state diagram (figure 1), the line of the boiling point of melts at 100 Pa is in the field of liquid solutions, at a concentration of ~ 20 – 60 at. % Pb in the L₁ + L₂ delamination region, less than ~ 10 at.% in the (Cu) + L two-phase region. At a pressure of 1 Pa, the boiling curve of the melt is placed in the field (Cu) + L, and the composition of the liquid phase corresponds to the composition of the melt at the intersection point of the liquidus curve ~ 94 at. % Pb.

![Figure 1. Copper-lead system state diagram.](image1)

![Figure 2. Copper-zinc system state diagram.](image2)

That is, the evaporation of lead will proceed from an alloy rich in its content. As the lead evaporates at 1 Pa, only the quantitative ratio of the (Cu) and L phases will change. Based on the position of the boundaries of the vapor-liquid equilibrium fields, technological difficulties in the distillation separation of lead from copper are not expected. The vapor phase will be almost entirely lead.
In the Cu - Zn system (figure 2), the region of existence of liquid solutions at atmospheric pressure between the liquidus line and the boiling curve is not large in temperature, especially in the region of concentrations corresponding to the composition of brass. Boiling points in vacuum are superimposed on the regions of ε, γ, β, Cu3Zn, (Cu) solid phases existence and their solutions. Only at a pressure of 100 Pa, the boiling curve of the melts intersects the low in copper concentration liquid field (L), and the two-phase field (ε + L). The transfer of zinc into the vapor phase from its alloys with copper will be a sublimation process mainly from crystalline phases, which significantly reduces the technological intensity of the separation process.

The process of evaporation of zinc from liquid solutions with copper under equilibrium conditions in a forevacuum is possible only at a very low concentration of zinc - 0.51 and 1·10⁻³ % at 100 and 1 Pa, respectively. The process of zinc evaporation from the melt needs a significant increase in pressure over the liquid bath. The melting point of even brass rich in zinc content (up to 30%) is close to the boiling point of zinc at atmospheric pressure (907°C). Consequently, the evaporative extraction of zinc during the melting of such a metal concentrate is possible only at atmospheric pressure. At the same time the vapor phase will be represented by zinc by more than 99.9%.

Two schemes of separating the concentrate metals can be considered while analyzing the state diagrams at low pressure in the context of the distillative separation of components. The first of them includes the separate extraction of zinc by distillation at atmospheric pressure and the subsequent extraction of lead by distillation in a forevacuum with separate condensation of zinc and lead (in two condensers) and the accumulation of copper in the still bottoms. The second is the joint evaporation, first, mainly of zinc, then lead and zinc with a slow decrease in pressure from atmospheric to forevacuum and joint condensation of the vapor phase in one condenser.

The second option is supported by the possibility of obtaining lead with zinc impurity (up to 2%) and zinc with lead impurity (up to 1%) due to the separation of the collective condensate during vapor deposition in liquid form at a pressure of more than 30 Pa and a temperature of more than 420°C. As it follows from our earlier study [10], the subsequent possible re-evaporation of zinc from lead-zinc condensate will be largely prevented by a higher vapor pressure in the evaporation zone, by supplying steam to the condensation zone, which will shift the vapor (ZnV) → liquid (ZnL) reaction towards the formation of the liquid phase. However, based on the industrial practice of zinc vapor condensation, it is not possible to prevent the formation of a certain amount of zinc dust, due to solid-phase condensation in the volume and removal of the formed particles by the vapor-gas flow outside the condenser.

In addition to the problems associated with the vaporization of zinc and lead, there are difficulties in forming a molten bath to be separated by evaporation. When waste is incinerated, slags are formed, in which alloys melted particles of various compositions are distributed. According to preliminary data, during mechanical grinding of slag, films consisting of refractory compounds, including carbides and oxides, preventing coalescence with the melt molten bath are formed on the surface of particles, granules, less than 10 mm in size. The latter is a significant obstacle in the technical design of the still bottoms unloading process. In this regard, it seems expedient to pre-melt the polymetallic concentrate into rough brass, followed by the separation of metals by distillation.

For this reason, the metal concentrate is proposed to be processed with preliminary melting into rough brass, then (or simultaneously) first to distill zinc at temperatures above 1000°C with a gradual decrease in pressure from atmospheric to 30 – 300 Pa, which will ensure the subsequent distillation of lead, and joint condensation of the vapor phase in the same condenser. During the liquid-phase vapor condensation at temperatures above 420°C and pressures above 30 Pa, spontaneous separation of lead-zinc condensate by stratification in the liquid phase is possible.

3. In-process tests
Technological research on the processing of metal concentrate completed with preliminary melting into rough brass in the induction furnace with a controlled atmosphere (in argon) at a temperature of 1,000 – 1,100°C. In the process of melting onto rough brass, zinc evaporation up to 10-15% of its
amount in the concentrate was observed. The alloy separation by distillation performed in a vacuum electric furnace equipped with a crucible evaporator and a heated condenser, connected by a heated steam line.

The heated parts of the evaporator, steam line and condenser are made of quartz, the crucible evaporator is made of graphite. Collective condensate from the condenser was discharged into an unheated crucible. Distillation products were recovered from the vacuum furnace in solid form after filing it with an inert gas and cooling. The collective condensate was recovered and remelted in an argon atmosphere for separation into zinc and lead layers. The processed products were weighed and analyzed. The amount of lead and zinc condensate was calculated without dividing the collective condensate ingot: by the volume of the layers and the density of metals – zinc and lead. The composition of the ingot layers has been tested, the lead layer was tested from the bottom part, the zinc layer was tested from the surface. The tests have basically confirmed the correctness of the selection of technological conditions and parameters with obtaining the expected results.

As an example of the distribution of metals during vacuum distillation of rough brass, the balance (table 1) of vacuum melting at a temperature of 1,000 – 1,050°C for 4 hours with a slow decrease in pressure from 92 kPa (690 mm Hg pressure at the Almaty level) up to 30 Pa at the end of the process. The evaporation area is 1.13·10⁻² m².

| Balance items       | Weight Kg | %  | Zinc Content, % | Distribution, % | Lead Content, % | Distribution, % |
|---------------------|-----------|----|-----------------|-----------------|-----------------|-----------------|
| Loaded: Rough Brass | 3.130     | 100| 16.60           | 100             | 4.07            | 100             |
| Produced: Rough Zinc| 0.530     | 16.93| 98.70          | 102.14          | 0.95            | 3.95            |
|                    | 0.126     | 4.03| 1.74            | 0.42            | 96.35           | 95.29           |
|                    | 2.431     | 77.67| 0.22            | 1.04            | 0.21            | 4.01            |
|                    | 3.087     | 98.63|                | 103.60          | 103.25          |
|                    | -0.043    | -1.37|                | +3.60           | +3.25           |

| Balance items       | Weight Kg | %  | Copper Content, % | Distribution, % | Tin Content, % | Distribution, % |
|---------------------|-----------|----|-----------------|-----------------|---------------|-----------------|
| Loaded: Rough Brass | 3.130     | 100| 77.40           | 100             | 1.80          | 100             |
| Produced: Rough Zinc| 0.530     | 16.93| 5·10⁻⁴         | 1.1·10⁻²        | 5·10⁻⁴        | 0.47            |
|                    | 0.126     | 4.03| 2·10⁻⁴         | 1.0·10⁻⁵        | 5·10⁻⁴        | 0.11            |
|                    | 2.431     | 77.67| 97.01          | 97.44           | 2.14          | 92.40           |
|                    | 3.087     | 98.63|                | 97.45           | 92.98         |
|                    | -0.043    | -1.37|                | -2.55           | -7.02         |

It is apparent that zinc and lead with high recovery are taken out into rough middlings. The still bottoms in the form of rough copper, can be processed by electrolysis in copper production.

4. Conclusion
Based on the above results, inference should be drawn that it is possibility in principle to separate the polymetallic concentrate into separate products: zinc and lead condensates – rough metals and still bottoms, where copper is concentrated, which, after refining, can be sold as commercial products. It
should be noted the high recovery of each of the metals in the middling product of the same name. At the same time, the processing technology and the flow chart design should be significantly refined.

Acknowledgments
This research was completed with the financial support from by the Ministry of Education and Science of the Republic of Kazakhstan (grant AR 08855494).

References
[1]  Kirillov A, Slavin A M and Şişigina T N 2005 Modern high technologies 5 68. http://top-technologies.ru/ru/article/view?id=22945 (in Rus.)
[2]  Friedrich B 2019 Conference: Workshop “Norwegian-German Business Cooperation” http://dx.doi.org/10.13140/RG.2.2.12328.83207 (in Eng.)
[3]  Gisbertz K and Friedrich B 2015 Conference: Berliner Konferenz: Mineralische Nebenprodukte und Abfälle - Aschen, Schlacken, Stäube und Baurestmassen (Berlin/Germany) http://dx.doi.org/10.13140/RG.2.2.17194.21443 (in Eng.)
[4]  Welcome to the supersort®technology DHZs processing technology for MSWI bottom ash and shredder residues https://www.supersort.ch/en/ (in Eng.)
[5]  Malyşev V P, Turdukojaeva A M, Ospanov E A and Sarkenov B 2010 Evaporation and boiling of simple substances (M.: Nauchnyi mir) 293–8 https://www.twirpx.com/file/2378796/ (in Rus.)
[6]  Trebukhov S A, Volodin V N, Ulanova O V, Nitsenko A V and Burabaeva N M 2021 Kompleksnoe ispol’zovanie mineral’nogo syr’a 1 (316) 82–90 https://doi.org/10.31643/2021/6445.10 (in Eng.)
[7]  Dai Y N and Yang B 2000 Vacuum Metallurgy of Non-Ferrous Metals (Beijing: Metallurgical Ind. Press) 3 516–43 (in Eng.)
[8]  Timuçin M 1980 Metall. Trans. 11B 3 503–10 (in Eng.)
[9]  State Diagrams of Binary Metallic Systems: A Handbook. ed. Lyakişeva N P (M.: Maşinostroenie) 2001 3 1 872 p http://www.vixri.com/?p=4635 (in Rus.)
[10] Volodin V N, Khrapunov V E and Marki I A 2011. Russian Journal of Physical Chemistry A. 85 7 1285–7 https://doi.org/10.1134/S0036024411070363 (in Eng.)