A novel method of waste processing of polymetal raw materials to make useful nanoproducts

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Abstract. The article deals with the theoretical basis of polymetal waste processing in chloride solutions. A schematic diagram is proposed for the processing of polymetal raw materials in a closed cycle. According to this scheme, the possibility is shown of obtaining metal products with highly developed nanostructure.

1. Introduction

Constant depletion of polymetal raw materials leads to the need of developing new technologies for their processing \cite{1, 2}. Existing pyrometallurgical technologies are extremely energy-consuming and labor-intensive, and do not meet modern environmental requirements, especially for the disposal of industrial waste \cite{3-5}. Hydrometallurgical technologies are not only more environmentally friendly in comparison with others \cite{1, 2, 6}, but also allow to carry out complex processing of metal-containing raw materials. This is confirmed by the study of these raw materials by various methods (X-ray, optical, nuclear magnetic, etc.). Devices based on these methods are successfully used to solve various problems \cite{7-13}.

One of the promising directions of processing raw materials containing heavy non-ferrous metals is the use of special solutions involving the amazing properties of complex compounds \cite{14-16}.

2. A new method and a block diagram of the technological process

It is known that the complexation significantly changes the solubility of low-soluble substances under normal conditions. In the world, there are quite contradictory opinions characterizing PbCl\textsubscript{2} as "completely insoluble salt in water" \cite{15, 17}, however, the interaction of Pb\textsuperscript{2+} with Cl\textsuperscript{-} occurs consistent formation of compounds: PbCl\textsuperscript{+}, PbCl\textsubscript{2}, [PbCl\textsubscript{3}]\textsuperscript{-}, [PbCl\textsubscript{4}]\textsuperscript{2-}, characterized by the stage stability constants \(K_1, K_2, K_3, K_4\).

The total solubility \(S\) is determined in this case by the sum of the concentrations of all lead-containing forms:

\[ S = \frac{K_{sp}}{\chi} \left[ \frac{1}{[Cl^-]^2} + \beta_1 [Cl^-] + \beta_2 [Cl^-]^2 + \beta_3 [Cl^-]^3 + \beta_4 [Cl^-]^4 \right]. \]  

(1)
where: $K_{sp}$ is the solubility constant, $\beta_i$ is the general stability constant ($\beta_i = K_1 \cdot K_2 \cdot \ldots \cdot K_i$), $\gamma_\pm$ is the average activity coefficient.

Knowing $\beta_i$, $K_{sp}$, $\gamma_\pm$ and [Cl$^-$], we can calculate the solubility of PbCl$_2$ taking into account the complexation. Thus, if at 20 °C the solubility of PbCl$_2$ in ordinary water according to the data is 1.06 %, then at a chloride concentration of 12.5 mol/dm$^3$ the solubility of PbCl$_2$ will be 2.58 % at 20 °C and 7.8 % at 108 °C.

All of the above applies also to silver chloride, bismuth, copper and other metal chlorides forming stable chloride complexes. In addition, metals (for example copper) in the formation of complex compounds can be dissolved in chloride solutions with the release of hydrogen:

$$\text{Cu} + 4\text{HCl} = 2\text{H}[\text{CuCl}_2] + \text{H}_2\uparrow.$$ (2)

In this case, due to the complex formation of their redox potential is shifted to the electro-negative area. Thus, salts of silver, lead, bismuth, slightly soluble salts of copper (I) and metallic copper and other metals can be dissolved in chloride solution. The insoluble residue must contain platinum group metals and gold.

For the successful conduct of dissolved chloride is currently used in practice solutions of calcium chloride (CaCl$_2$) as they allow reaching in a solution of higher concentration of chloride than, say, solutions of sodium chloride NaCl (see, e.g., French patent N 2495640 I PC C 22 B 3/00, C 01 G 5/00, 1982, this method includes selective leaching of lead and silver from waste by treating them with acidified CaCl$_2$ solution, followed by the separation of metals from the solution by cementation with aluminum).

Nevertheless, as a result of our research, an even more interesting chloride system was found, using solutions of zinc chloride ZnCl$_2$, which allows to increase the "chloride background" by 2-3 times in comparison with solutions of CaCl$_2$. Due to this fact, the solubility of insoluble compounds can also be significantly increased.

Advantage of the use of concentrated zinc chloride solutions for dissolving polymetal raw materials is evidenced by the fact that such solutions have an elevated boiling point; as was found in our studies, 10 M ZnCl$_2$ solution boils at 136 °C, while 4.5 M CaCl$_2$ solution boils at 108 °C. Increasing the temperature of the solution significantly accelerates the intensity of the leaching process (figure 1).

![Figure 1. A dependence of a leaching degree of slime on a time of dissolution.](image)
Metals, passing into chloride solutions, are in these solutions in the form of stable chloride complexes. Selection of these metals by such methods as chemical deposition in the form of slightly soluble compounds, sorption, extraction, is difficult and has seldom application. It was found that a fairly complete separation of metals can be carried out using the so-called "cementation" which includes the exchange reaction with some active metals. In this case, it is advisable to use zinc as an active metal, since in the case of ZnCl₂ solution, this opens up the possibility of creating a closed technology. The block diagram of the technological process for obtaining pure metals in the form of nanotubes is presented in figure 2.

![Block diagram of the technological process](image)

**Figure 2.** The basic technological circuit of polymetal raw (slimes) processing with reception of pure (clean) metals.

Preliminary experiments have shown that this process must be carried out automatically. This allows improving the quality of chemical processing and more accurately controlling the time of chemical reactions. For control and monitoring of technological processes it is more expedient to
use fiber-optic systems that have proven themselves to solve many complex technical and scientific problems [18-22].

3. Experimental results and their discussion
In figure 3 as an example, the structure of the silver sponge after the technological cycle is presented. It obtained by high-resolution electron microscope. We have found that the metals obtained by this technology are formed in the kind of nano-sponges:

Figure 3. Silver sponge under electronic microscope. The places of "accretion" (1) of particles of silver (2) are visible.

The analysis of the results confirmed our assumption that metals are formed in the kind of nanotubes. The study of these new nanostructured compounds is a rather complex process, which should be carried out by non-destructive methods, such as nuclear magnetic resonance [23, 24] or electron-optical force microscopy. The latter one is actively used in the study of new structures in green energy [25, 26].

Presumable mechanism of "coalescence" of silver particles (figure 3) can be explained by the presence of silver on the surface, located in HCl, AgCl thin films that can decompose with the release of silver.

4. Conclusion
The pure metals obtained in the form of nanotubes as a result of the experiments have increased conductivity and a lower degree of oxidation compared to the previously obtained elements. This makes them extremely attractive for use in electronics and nanoelectronics. The studies of production wastes of pure metals, obtained by our novel technology, conducted by ecologists under the leadership of academician of RAS Mikhail Fedorov, showed the absence of compounds dangerous for living organisms. This makes it possible to place the waste in open areas before further processing or to dispose of it immediately.
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