

## Conference Paper

# Extraction of Non-ferrous Metals from Underspoil Waters

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## Abstract

The focus of the study was the acidic underspoil waters of Safyanovskaya copper JSC containing 0.17 g/l of copper and 1.8 g/l of zinc (pH 2.8–2.9). The purpose of the work was research and development of water purification technology from impurities (copper, zinc, aluminum, iron, manganese), suggesting the possibility of copper and zinc extraction in the form of commercial products. The process of copper extraction by cementation with metallic iron was studied. It was shown that this method could allow to extract 94–95 % copper into a concentrate. The zinc extraction from solution after copper removal was studied by precipitation with NaHS, Na<sub>2</sub>CO<sub>3</sub>, NaOH and CaO. For economic reasons it is recommended to make zinc precipitation in two stages with CaO in order to produce cake containing 15–21 % Zn with extraction 80–87 %. This cake can be utilized at zinc processing plant. A process flowsheet for acidic underspoil waters, including copper cementation and the precipitation of zinc cake, has been developed. According to this scheme, mother liquor from zinc precipitation should be treated with lime until pH reaches 10–10.5, followed by pulp settling. As a result, purified water of the following composition is obtained, mg/l: zinc – 0.05, copper – 0.01, aluminum – 0.02, iron – 0.02, manganese – 0.05.

**Keywords:** underspoil water, copper, zinc, iron, cementation, calcium oxide, concentrate, precipitation.

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## 1. Introduction

The underspoil and mine waters of enterprises engaged in the processing of copper-zinc pyrite ores are an important resource for the extraction of copper and zinc in the Ural region. Traditionally, these waters are sent to neutralization plants, where non-ferrous and ferrous metals are precipitated with water regeneration for industrial needs. Thus, the extraction of valuable components is not performed. At the same time, the organization of water purification from impurities with the associated commercial extraction of valuable components may be appropriate. The aim of the study was to develop a process of copper and zinc extraction from underspoil waters in the form of commercial products.

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## 2. Results and Discussion

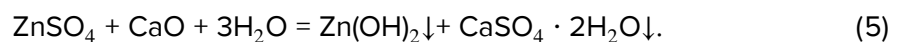
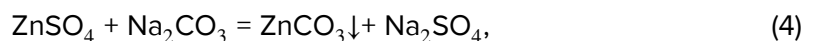
The object of the study was acid underspoil waters of Safyanovskaya copper JSC. The main valuable raw materials of these waters were copper and zinc. The initial solution had the following composition (according to the analytical laboratory of Uralmekhanoobr JSC), g/l: 0.168 Cu, 1.71 Zn, 1.65 K, 0.05 Na, 4.20 Mg, 0.84 Al, 0.23 Fe(III), 0.21 Mn, 0.60 Ca. pH of solution was 2.8–2.9.

In this work the extraction of copper and zinc in the form of insoluble substances was developed. Extraction of copper was carried out by cementation with an iron according to the equation [1]



It was necessary to obtain a copper concentrate with a minimum copper content of 15 % that satisfied the grade KM7 according to GOST R 52998–2008. Zinc concentrate according to GOST 5492–2012 must contain at least 45 % zinc. At the same time, in accordance with works [2, 3] it was pointed out that effective processing of zinc products by Waeltz process was possible while the content of the zinc in concentrate was at least 15–20 %. Therefore, in order to obtain zinc precipitates a wide range of available precipitating reagents was used, as follows: sodium hydrosulfide, sodium hydroxide, soda, lime.

Processes of precipitation proceeds with the following equations in accordance to [4]:



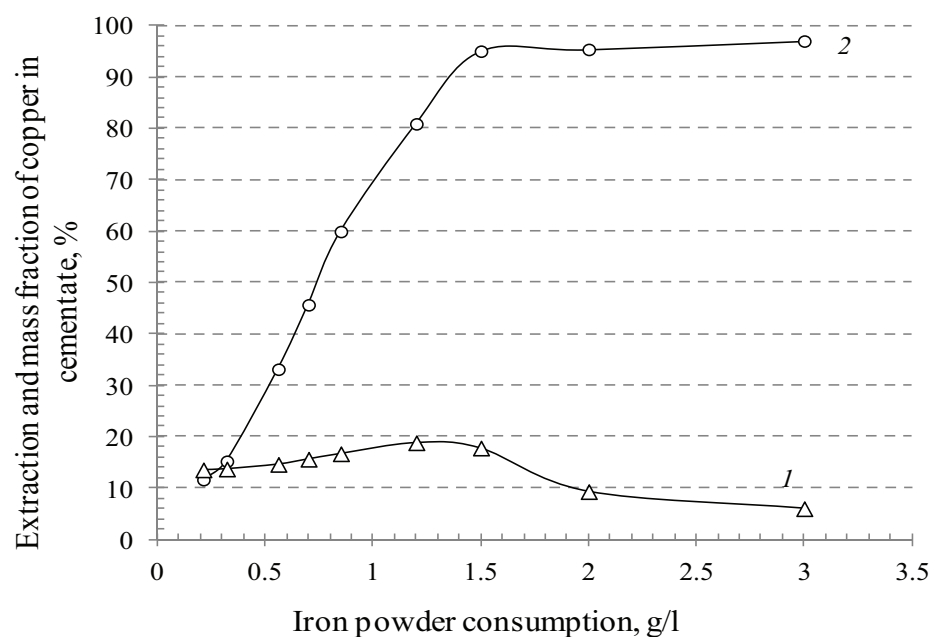
It was proposed to carry out cementation in two ways. The first method involved the use of reactor where iron powder was administered during stirring. Iron powder was produced in large quantities by spraying metal under pressure. In compliance to the first method, commercial powder of minus 200  $\mu\text{m}$  size was used. Cementation was carried out in a laboratory reactor with a capacity of 2 liters.

The second method was cementing on a jiggging machine with iron scrap loaded on sieves. It was assumed that when acidic water is supplied to pulsating sieves loaded

with scrap, copper cementation would occur with subsequent cleaning of the scrap surface from the resulting copper. In this case, copper would be partially collected in the concentrate collector and discharged together with mother liquor in the form of fine slurry. For cementation, a laboratory jiggging machine with movable sieves of the MOD-0.02 SKL brand was used. Machine was equipped with 2 sieves with sieving area of 10 cm<sup>2</sup> each. Iron scrap with a specific surface area of 0.2–0.6 m<sup>2</sup>/kg was used as a cementing agent.

While carrying out the cementation process with iron powder, the effect of powder consumption and the duration of cementation were studied. It was found that the optimal duration of the process is 0.5 hours. The optimal consumption of iron is 1.5 g/l, which one can see from the data presented in Figure 1. This was ensured by obtaining solutions with a copper content of 5–10 mg/l, while the extraction of copper to concentrate was 94–97 %.

While carrying out cementation on a jiggging machine, the aim was to select such conditions that would ensure stable production of a minimum concentration in the mother liquor over time. We studied the effect of mortar feed rate, scrap loading mass and chamber pulsation frequency on cementation rates. In the optimum mode found, about 350 l of the solution was processed. The copper content in the mother liquor deposition could not be obtained below 30 mg/l (corresponding to a recovery of about 82 %).



**Figure 1:** The influence of the iron powder consumption on the content (1) and extraction (2) of copper in cementate

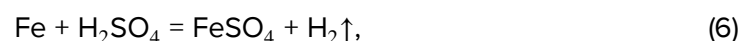
The phase composition of the optimally prepared and water-washed cementates was determined by the X-ray diffraction method using a XRD 7000 Shimadzu diffractometer. The composition is shown in Table 1. The data in Table 1 explains why low recovery is achieved using the jiggling machine. Obviously, a higher recovery is achieved with an excess of iron in the system, which is easily controlled by introducing an excess of iron powder into the pulp. In the jiggling machine the cementate is separated from the scrap and carried out in a stream.

TABLE 1: Phase composition of cemented copper

Substance	Material composition of precipitate obtained by various cementation modes, %wt.	
	using iron powder	using scrap in jigger
Metallic iron	36	5
Metallic copper	18	27
Basic aluminum sulfate	27	53
Cuprospinel	8	4
Goethite	5	5
Bassanite	4	4
Wustite	2	2

As a result, the content of excessive metallic iron in cemented copper obtained in the jigger is less than that obtained one using iron powder in reactor.

The resulting cementate is significantly diluted with unreacted iron, as well as with precipitated aluminum and calcium sulfates (bassanite), which are not removed during subsequent washing. Cementation is characterized by an increased specific consumption of iron for chemical reactions, corresponding to at least 7.0–7.5 kg per 1 kg of copper. This consumption is explained by the occurrence of side processes in accordance with the stoichiometry of reactions:

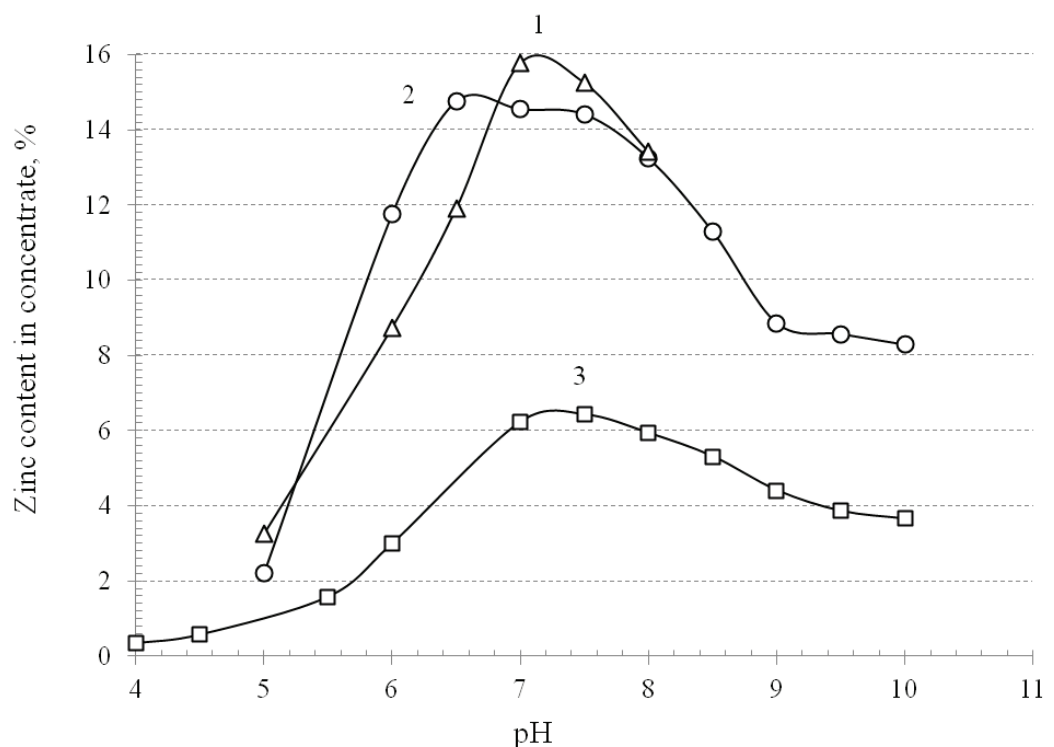


Zinc was developed from copper purified solution of the following composition, g/l: 0.01 Cu, 0.05 Fe(III), 1.30 Fe(II), 1.8 Zn, 1.5 K, 0.05 Na, 3.98 Mg, 0.60 Al, 0.18 Mn, 0.64 Ca. When zinc precipitation with sodium hydrosulfide was developed a precipitate was obtained with a zinc content of up to 49–51 % with an extracting of zinc 99 % from the solution. However, it was not possible to solve the problems of sludge dewatering: when pressure filtration in a Labox 25 laboratory unit at an injection pressure of up to 1.6 MPa was carried out the solid phase did not stop at all on the tested tissues. This can be explained by the fineness of the sediment, the size of which was 90 %

of the class minus 2  $\mu\text{m}$  according to data obtained from the Helos laser composition analyzer. Therefore, precipitation of zinc sulfide is not recommended due to practical considerations.

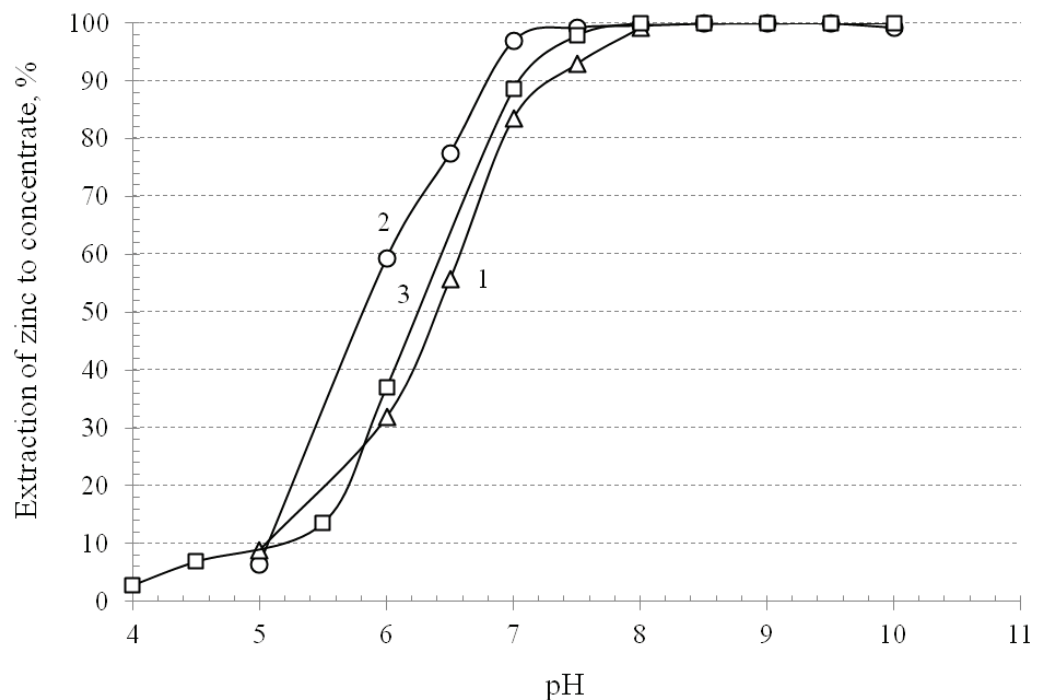
Figures 2 and 3 show the results of zinc precipitation with 10 % sodium hydroxide, 10 % soda and 10% lime suspension.

While precipitation with soda and sodium hydroxide was developed it was possible to obtain precipitates with a zinc content of 14–16 %. Specific consumptions were the following (per 1 kg of zinc):  $\text{Na}_2\text{CO}_3$  – 17.7 kg/kg,  $\text{NaOH}$  – 7 kg/kg. With the use of  $\text{CaO}$  it was possible to obtain a zinc content of up to 6.3 % with a specific consumption of 5.1–5.3 kg/kg. Due to commercial considerations it was recommended to use  $\text{CaO}$ .



**Figure 2:** Zinc content in concentrate depending on pH:  $\text{Na}_2\text{CO}_3$  (1),  $\text{NaOH}$  (2),  $\text{CaO}$  (3)

Further studies have shown that zinc precipitation is better to be accomplished in two stages. Initially, lime cleaning of the solution from aluminum is carried out at pH 5.0–5.5 to obtain a dump cake. Further, a zinc product is obtained from the solution at a pH of 7.5–8.5. As a result, precipitates with higher zinc content (15–21 %) are obtained with the extraction of 80–87 %. The resulting precipitates are well filtered (specific filtration rate under vacuum was 0.7–0.8  $\text{t}/(\text{m}^2 \cdot \text{h})$ ). After filtration and drying, the precipitates can be disposed of at zinc processing plants. It is recommended to treat water after zinc removal with lime until pH of 9.5–10.5 is reached and, after settling in settling ponds,



**Figure 3:** Extraction of zinc to concentrate depending on pH: Na<sub>2</sub>CO<sub>3</sub> (1), NaOH (2), CaO (3)

send it into circulation for technological use. It is shown that this pH range is optimal for deep cleaning of non-ferrous metal impurities. Final water after all stages of treatment is characterized by following composition, mg/l: 0.05 Zn, 0.01 Cu, 0.02 Al, <0.02 Fe, 0.05 Mn.

### 3. Conclusions

It is founded that extraction of copper from underspoil water is advisable to accomplish in the form of copper cementate in case of the presence of cheap source of iron.

The most economical way of separating zinc from decontaminated underspoil water is to precipitate it with lime in the form of a hydrated cake.

After the release of zinc, the mother liquor is recommended to be sent to the existing neutralization station. It is recommended to carry out neutralization up to pH 10–10.5 in order to maximize purification from non-ferrous metals (copper, zinc, manganese).

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