

# New approaches to hydrometallurgical processing of low-grade mineral and technogenic raw materials of Kazakhstan

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## Abstract

The given research work is focused on development of knowledge about possibilities of circular flows turnover that occurs when low-grade raw materials are processed. According to a number of indicators, low-grade raw materials are close to technogenic formations. Basing on the identified mutual interactions of different technological factors it has been suggested to converse semi-products of hydrometallurgical processing of low-grade and technogenic materials of zinc production into valorization.

Nowadays zinc plants involve low-grade concentrates into processing by the method of atmospheric leaching. The resulted solutions contain increased number of ions  $Fe^{+2}$  and  $Fe^{+3}$ . The conducted researches proved that in order to achieve required permissible concentrations of the indicated impurities, it is necessary to include the following operations into processing procedure: deposition of ions  $Fe^{+3}$  contained in the solution, electrochemical oxidation of ions  $Fe^{+2}$ , final purification of the solution from iron with the help of complexons – nitrile-trimethylene-phosphonic acid, cementing purification from copper ions. The formed iron complexonates residues (after drying) can be used as semi-product at ferrous metallurgical enterprises for production of valuable iron-phosphoric alloy.

The results obtained at the given stage can be of economic and industrial interest for hydrometallurgical production of non-ferrous, rare, and disseminated metals of Kazakhstan, Russia, and other countries. These countries are currently engaged in problems of processing of low-grade mineral and technogenic raw materials. However, up-to-date technologies are oriented only on base metals such as Ni, Zn or Cu, and remaining part of the material is left unused. Development of new effective approaches to hydrometallurgical processing of low-grade mineral and technogenic raw materials of Kazakhstan will enable considerably to reduce amount of mined raw materials due to involving accumulated technogenic materials, to decrease ecological burden on the environment, to increase complexity of mineral raw materials use. Besides this will create prerequisites for the development of circular economy with an emphasis on wastes management and valorization of enterprises resources.

**Key words:** purification, iron, copper, nitrile-trimethylene-phosphonic acid, zinc dust.

## 1. Introduction

According to the data provided by some analysts, world demand for metals and use of resources in the period between 2010 and 2030 must double (Kinnunen and Kaksonen, 2019). The author notes that as demand increased, at the same time quality of feedstock for mining industry declined every year. This causes not only ecological problems due to accumulation of wastes amount such as tailing dumps and others, but also has economic and social effect. The term “tailing dump” represent remains of mine rocks and technologic solutions after recovery of precious minerals from mined ore. Metallurgic industry of the Republic of Kazakhstan is the motive power for the economic development of the whole country. So it is very urgent to create and develop circular economy with an emphasis on wastes management and valorization of enterprises resources. Tails valorization means recovery of residual materials and utilization of mineral matrix.

Traditionally, when native polymetallic raw resources containing lead, zinc, copper and a number of precious and rare metals are processed, selective lead, zinc and copper concentrates are produced after pre-concentration. Other precious component are distributed in these concentrates. Although the period of raw materials pre-treatment before processing is very long, it is nearly impossible to achieve complete separation of ore components. This is the reason why the produced selective concentrates contain considerable amount of impurities (Zn impurities in lead concentrate, Cu impurities in zinc concentrate etc.).

Hydrometallurgical procedure of sulphide zinc concentrates processing is widely used. It includes the following stages: oxidizing roasting → leaching → electrolysis and enables simultaneously recover impurities of copper, cobalt, cadmium, and a number of rare metals into semi-products which are further produced in market condition. As current semi-products, accumulated technogenic wastes and off-balance low-grade types of raw materials are involved into processing, complete upgrade is required, as well as adaption of technological regime and other innovations.

Object of the given research is simulated sulfate zinc solutions produced during hydrometallurgical processing of low-grade mineral and technogenic raw materials. The goal of the research is to define optimal parameters of zinc solutions purification, filtration and electrolysis processes. The zinc solutions are characterized by high iron content as they were formed during atmospheric leaching of off-balance zinc raw materials

## 2. Analysis of the problem state

Technology of zinc concentrates processing including high-temperature roasting – slag leaching – electroextraction – is commonly used technology. Purified solution that is supplied on the stage of electroextraction is of high sensitivity to such impurity as iron. Iron in zinc electrolyte negatively affect current output and quality of cathode zinc (Karimov et al. 2017).

The parameters regulating iron removal from acid leaching solution during «goethite» process were identified and were studied in 80-s of the XX century (Davey and Scott, 1976). Two variants of the process, namely Vieille Montagne and Electrolytic Zinc have been researched. The degree when cations (Ni, Co, Cu, Zn, Mn) and anions ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) are carried away along with iron deposit have been determined under the controlled conditions.

Development of Goethite and Jarosite processes enabled to remove high iron concentrations from solutions of metal sulphites that are easily separated in crystal forms. This enabled economically to recover zinc from raw material containing iron, especially from zinc ferrite that is usually formed during roasting of zinc concentrates. Processes appeared to be easily adapted for meeting certain requirements of different leaching procedures that were used at zinc plants that operated before. The processes also enabled to project new zinc plants that provide higher economic returns from elegantly simple technological processes (Gordon and Pickering, 1975).

However, depletion of non-ferrous and rare metals easy ores including zinc, is evident all over the world, in particular in Kazakhstan. The depletion causes involvement of low-grade concentrates containing metals into the process of metallurgic processes. When such concentrates are processed by hydrometallurgic method solutions are formed. The solutions are characterized by high content of impurities especially iron. Iron is present in solutions in divalent and trivalent states. Processing of such solutions is rather problematic nowadays. Technological aspects of sulphate solutions purification from iron is considered in some detail in special literature however, some theoretical issues concerning oxidation and hydrolysis in multicomponent solutions require attention.

Claassen et al. (2002) found out that the process of iron removal from para-goethite (PG) is one of several deposition processes that are used for iron removal from zinc concentrated technological solutions. It was found out that iron distribution in iron containing residuals of Zincor process is as follows: about 50 % of iron is in combination of schwertmannite and ferrihydrite, 20 % as jarosite, 25 % as franklinite and trace amounts of pyrite, and 5 % of unknown phase. Iron is mostly removed as poor crystallized intermediate iron phases and depends on profile of specific pH used when iron is removed and silicon dioxide is co-deposited (Claassen et al., 2002).

Later this author (Claassen et al., 2006) noted that during continuous supersaturation in continuous crystallizer pan, agglomeration of metastable iron phases depends on pH, temperature, iron concentration in solution, stirring rate, solution viscosity and other parameters. Filtrability of the formed solid particles has been studied and efficiency of iron removal by using Hadamard matrix has been assessed.

Dyer et al. (2012) carried out the research on co-deposition of iron and earth silicon oxides from acid solutions thus simulating para-goethite process, stage of iron removal used in zinc hydrometallurgy. Laboratory experiments on continuous crystallizing were carried in the conditions used in the production, when pH (85 °C) was maintained at 2.65 level, Fe and Si combined concentration was 0.1128 M and Si:Fe molar ratio varied from 0 to 0.43. It was shown that degree of silicon dioxide polymerization to deposition reaction defines co-deposition mechanism and consequently, properties of the residual. When polymerized earth silicon is present less dense aggregates with smaller average particles size are formed and this has negative influence on dehydration. In contrast, when earth silicon is enabled to polymerize before the reaction of iron deposition, most part of earth silicon is removed from solution. As these effects are keys to effective deposition stage in the process, influence of earth silicon polymerization should be taken into account in operations with high silicate concentrates (Dyer et al., 2012).

Beside silicon oxide impurities, copper compounds have big impact on the process of purification of sulphate zinc solution. For example, in the work of Zaabar et al. (2013) copper cementation in acid sulphate solutions was carried out in the presence of nettle extract (*Urtica Dioica* L.). It was shown that cementation rate increase when temperature rises up to 37 °C, and it is improved due to increase of stopping agent concentration (nettle extract) up to optimal value  $1.5 \text{ g}\cdot\text{l}^{-1}$ .

The authors Ahmed et al. (2011) studied copper cementation from sulphate medium with the use of zinc ash and determined that about 99 % of copper can be recovered from sulphate solution, when initial pH = 2. Solid:liquid ratio is 0.05 after 30 minutes of non-stop shaking.

The process of hydrolytic iron deposition from simulated leach solution of nickel lateritic atmospheric leaching described in the work of Mbedzi et al. (2016) is of certain interest for detecting mutual influence of

equilibrium value pH, temperature and addition of oxidizing component on total iron content (bivalent iron (Fe (II)) and trivalent iron (Fe (III))), as well as aluminum, chromium, nickel, and cobalt in deposit. Systematic variations of experimental variables showed, that  $\geq 99\%$  of trivalent iron can be removed from solution under conditions similar to those that were used during standard partial neutralization when zinc and nickel are produced, pH is 2.5, temperature is less than  $100^\circ\text{C}$  and with minimal losses ( $< 0.5\%$ ) of both nickel and cobalt. It has been found out that increase of temperature from  $55$  to  $90^\circ$  doesn't have significant impact on Fe (III) deposition value, but caused considerable increase of aluminum removal from  $67\%$  to  $95\%$  and improved filtrability of deposits. Deposition of bivalent iron wasn't observed even when pH was 3.75 and there was no oxidizing component that was removed ( $98\%$ ) by oxidizing deposition with gas oxygen when pH was 3.5. Unlike Fe (III) deposits, operating temperature influences considerably oxidizing deposition of Fe (II). Thus the authors came to the conclusion that in practice hydrolytic deposition and oxidation for iron removal should be carried out at  $85^\circ\text{C}$  in order to provide deposition of both bivalent and trivalent iron.

### 3. Materials and methods

The researches on hydrolytic deposition of trivalent iron ions from simulated sulphate zinc solutions were carried out in laboratory reactor made of boracium silicate glass (IKA LR-2.ST, Germany), volume -  $2\text{ dm}^3$ . Sulphate zinc solution containing  $\text{Fe}^{+3}$  ions (volume -  $1\text{ dm}^3$ ) was heated up to  $45\text{-}85^\circ\text{C}$ , then seeding agent was added and the solution was neutralized with calcium oxide until pH was about 1.1. As zinc oxide reacts with the solution more slowly than calcium oxide for example, it was charged by small portions every 20-30 minutes. The process was carried out with intensive stirring 120 minutes long the pulp was filtered in laboratory filter (drook-filter)  $55\Phi\text{T}$ , deposit was washed with water and produced cake and filtered material were analyzed on the content of iron, zinc and other components.

It is known that the most effective reagent for binding  $\text{Fe}^{+3}$  ions into low-soluble compounds is complexon of nitrile-trimethylene-phosphonic acid (NTPh). The complexon forms hardly soluble complexonates of the composition  $\text{Fe}_3\text{H}_3(\text{NTPh})_2 \cdot 6\text{H}_2\text{O}$  in acid medium. Its solubility is  $5.5 \cdot 10^{-5}\text{ g}$  in 100 ml of water, or  $9.85 \cdot 10^{-5}\text{ mol/dm}^3$  at room temperature, that is recalculated into  $\text{Fe}^{3+}$  ions is  $0.00792\text{ g/dm}^3$  or  $7.92\text{ mg/dm}^3$ .

Researches on electrochemical oxidation of  $\text{Fe}^{+2}$  ions were carried out on electrolyzer where anode and cathode space is separated by anion-exchange membrane. In operation with anode and cathode space separated with the membrane, purified model solution of iron was pumped through cathode space and circulation rate maintained the same for balancing pressure in anode and cathode chambers. Solutions after electrolyzer are supposed to be sent to basic technological procedure: from anode chamber to hydrolytic purification, from cathode chamber - to the operation of impurities cementation. In the course of experiments the following parameters were controlled: current force, circulation rate, initial content of elements. After anode oxidation of  $\text{Fe}^{+2}$  ions,  $\text{Fe}^{+2}$  ions were deposited according to procedure described above.

Experiments on fine purification from  $\text{Fe}^{+3}$  ions in opened reactor with a propeller mixer at room temperature ( $22\text{-}25^\circ\text{C}$ ). Solution of complexon- precipitator was prepared preliminarily in a separate volume. Solubility of NTPh acid is rather high accounting for 100 g per 100 ml of water that corresponds to concentration  $3\text{ mol/dm}^3$ . The choice of maximum concentration is due to preservation of water balance. Solution was dosed in droplets from special tube elevated over reactor level. Precipitate is formed immediately in the form of large flakes. The formed pulp was maintained by simultaneous mixing during 30-40 minutes for complete deposition. Every test served for defining complexon consumption, residual iron concentration at different pH and  $\text{Fe}^{3+}$ -initial concentrations.

After precipitate was formed, free filtration was carried out for defining its rate. Separately rate of precipitation free settling was determined. The process of defining filtration and settling rates provides characteristic assessments of deposits technological characteristics. Free filtration rate was defined as change of filtered material amount per time unit through filters of similar porosity.

Tests on cementation purification of solutions from copper were carried out with sunk propeller mixer when it was intensively stirred (100 rpm) during 40-60 minutes at room temperature. Zinc powder was added by portions, zinc overconsuming over stoichiometric was 150-200%. Initial copper concentration and zinc powder consumption were varied. Residual concentration of copper was defined photometrically on spectrophotometer ПЭ-5400 УФ. Increase of zinc concentration in electrolyte was controlled by the method of trilonometry titration.

### 4. Results and discussion

Object of the given research work are model sulfate zinc solutions obtained by hydrometallurgic processing of low-grade and technogenic materials of zinc production.

#### 4.1. Hydrolytic precipitation of Fe<sup>3+</sup> ions

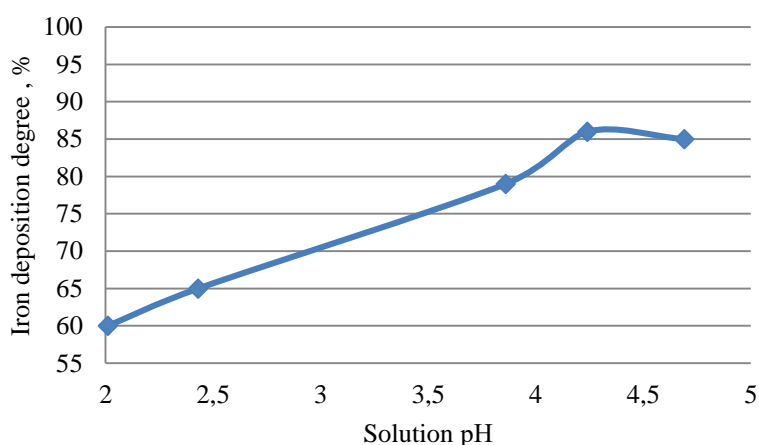
Tests were carried out with the use of experiment planning matrix described in the work. Factor levels of parameters optimization when large scale-laboratory tests on Fe<sup>3+</sup> precipitation from simulated sulphate-zinc solutions are provided in Table 1.

**Table 1**

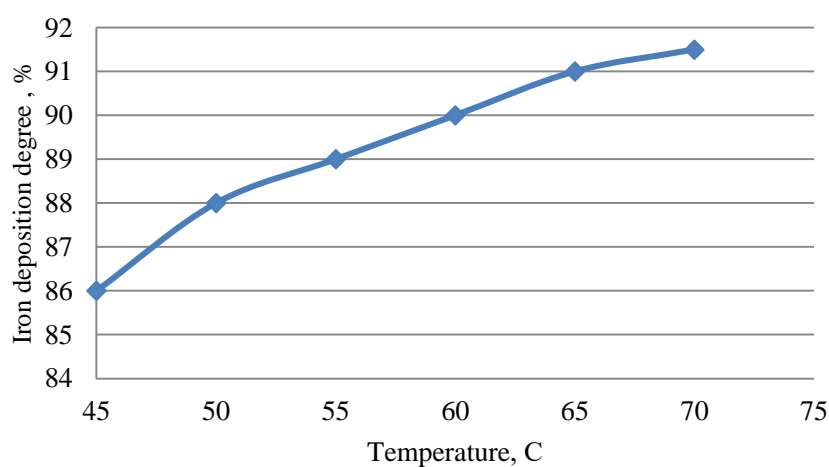
Factor levels of parameters optimization when large scale-laboratory tests on Fe<sup>3+</sup> precipitation from simulated sulphate-zinc solutions

№	Factor	Level of factor level	
		Maximum	Minimum
1	pH	4.69	2.43
2	Zn concentration, g/dm <sup>3</sup>	130	60
3	Fe <sup>3+</sup> concentration, g/dm <sup>3</sup>	15	8
4	Temperature, °C	80	30
5	Expense of seeding agent, g/dm <sup>3</sup>	100	10
6	Stirring rate, rpm	300	800

During the testing process it was found out that some factors influence iron deposition and characteristics of produced precipitates. Influence of pH and temperature on the degree of iron recovery is shown in Figures 1 and 2 respectively.



**Fig. 1.** Dependence of iron deposition degree on solution pH



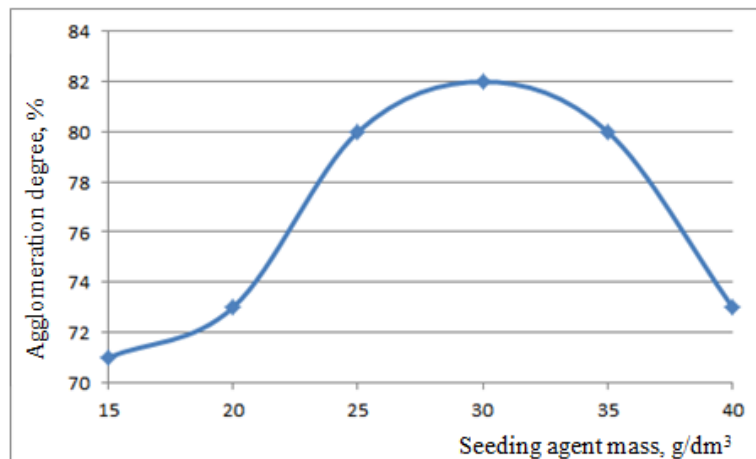
**Fig.2.** Dependence of iron deposition degree on solution temperature

When pH is 2.72 under conditions of minimal supersaturations on  $\text{Fe}^{+3}$ , large-crystalline precipitate of hydrogoethite is deposited. It has solubility product that equals  $4.4 \cdot 10^{-44}$ . Increase of pH and temperature up to 80 °C causes deposition of amorphous fine-dispersed hydrogoethite. It was found out that iron oxidation at high pH bring about conditions of considerable supersaturation in ferrite-ions.

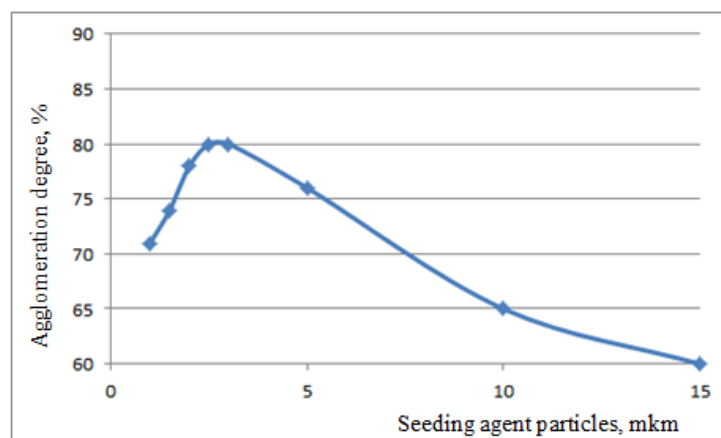
Maximal degree of iron deposition is observed when pH is in the interval 3.8-4.2 then it begin to decrease. It is supposed that this effect is observed due to the fact that when pH is 4.2 the number of active crystallization centers of hydroxy compounds is reduced and process is transferred into kinetic area where its rate is determined by diffusion limitations. From the other hand when the temperature is higher than 60 °C and pH is fixed the degree of iron deposition is increased considerably. Thus pH and temperature have evident influence on  $\text{Fe(III)}$  ions hydrolysis in several ways. First of all these factors define level of solution supersaturation with hydroxyl compounds that is driving force for formation of precipitations of certain structure and size.

Supersaturation in its turn affects the final size of the particles, distribution of particles size of the whole precipitation according to size and precipitation morphology, all this determines its filtration rate. It is known that small, low-dense particles were formed at high levels of solution supersaturation that takes place as a rule at low temperatures and high pH values and when iron initial concentration in solution is high. Positive influence of temperature on particles enlargement and formation of relatively large aggregates is probably connected with bigger difference of particles growth rates at higher temperatures. This influence provides higher probability of separate small particles aggregation. The obtained data proves the results of experiments provided in the work of Chang and Hourng (2001).

Influence of seeding agent initial mass and initial size of its particles on the degree of iron recovery into precipitate is shown in Figures 3 and 4.



**Fig. 3.** Influence of seeding agent mass on agglomeration degree (calculated in %) of metastable iron phase precipitates



pH=3.2, temperature 65 °C and stirring rate is 600 rpm from solution, containing 10 g/dm<sup>3</sup> Fe in the form  $\text{Fe}_2(\text{SO}_4)_3$  and 5 g/dm<sup>3</sup>  $\text{H}_2\text{SO}_4$ . 2.5% ZnO suspension was used as neutralizer .

**Fig. 4.** Influence of seeding agent particles initial size on the degree of agglomeration (calculated in %) of metastable iron phase precipitates

It is evident that optimal expense of seeding agent when maximal degree of newly formed precipitates of iron hydroxy compounds agglomeration is observed in the interval 15-35 g/dm<sup>3</sup>. The results provided in Figures 3 and 4 show that deposition degree goes through the maximum and then decreases when particles size is more than 3 mkm and seeding agent mass is more than 30 g/dm<sup>3</sup>. Optimal expense of seeding agent when iron hydroxides are settled is 25-30 g/dm<sup>3</sup> (for initial iron concentration 10 g/dm<sup>3</sup>).

The conducted tests enabled to formulate the following:

- solution pH has determining influence on the degree of Fe<sup>+3</sup> deposition from zinc containing sulphate solutions. The optimal range of pH has been defined that accounts for 3.7-4.25.

- optimal amount of seeding agent is 20-30 g/dm<sup>3</sup> for iron initial concentration, however, this factor can vary considerably depending on iron initial concentration, in solution, distribution of particles size and phase composition of seeding agent;

- increase of temperature higher than 60 °C has positive influence on both enlargement of precipitate particles and ultimate recovery of iron into precipitate in the form of oxyhydrate metastable phases.

#### 4.2. Electrochemical oxidation of Fe<sup>+2</sup> ions

After hydrolytic purification from Fe<sup>+2</sup> ions solutions are filtered and sent to electrochemical oxidation of Fe<sup>+2</sup> ions left in the solution. Electrochemical oxidation of Fe<sup>+3</sup> ions take place only in anode cell of electrolyzer that is separated from cathode cell by ion-exchange membrane. Its main purpose is to prevent iron ions from penetration to cathode.

The obtained results showed high efficiency of anode electrooxidation of iron in flow electrolyzer. Degree of Fe<sup>2+</sup> conversion into Fe<sup>3+</sup> is more than 99.9%. It's evident that copper contained in the solution have considerable and positive effect on decrease of residual Fe<sup>2+</sup> concentration in the solution. In the course of iron electrooxidation content of sulphur acid in the solution is considerably increased (from 22.3 to 25-38 g/dm<sup>3</sup>) as oxygen simultaneously precipitates on the anode. Growth of acid content in the solution is especially evident in experiments when current densities are high, where electricity consumption to iron oxidation and secondary reaction of water decomposition ratio is shifted to the latter.

Electric energy consumption is about 8-12 kWh /kg when current density is 250 A/m<sup>2</sup> it isn't higher than 22 kWh /kg when current density is 350 A/m<sup>2</sup>. Zinc and copper content in solution nearly don't change during anode oxidation of iron in a flow electrolyzer.

Minimal Fe<sup>2+</sup> concentration in final solution that is 50 mg/dm<sup>3</sup>, is obtained under the following conditions of flow electrolyzer operation: current density is 350 A/m<sup>2</sup>, rate of electrolyte supply is 4.4 dm<sup>3</sup>/h, copper content in the solution is 2.43 g/dm<sup>3</sup>.

#### 4.3. Fine purification of solution from iron with the help of NTPH acid

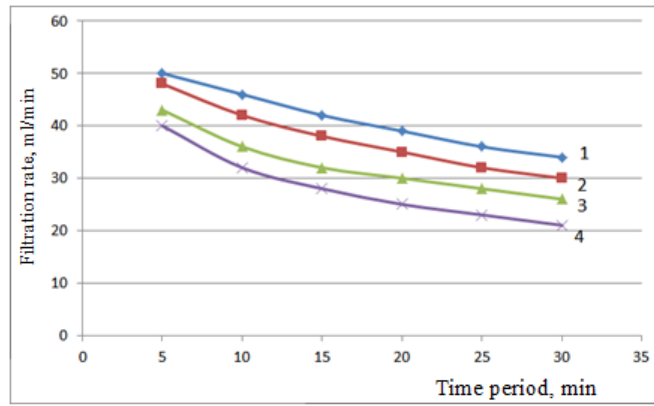
After hydrolytic purification of the solution from iron Fe<sup>3+</sup> residual concentration was 1-2 g/dm<sup>3</sup> in different series of experiments.

Then in order to achieve more effective deposition of residual amount of iron, new reagent (NTPH acid) addition into the studied system has been tested. The results of fine purification of electrolyte from Fe<sup>+3</sup> with the help of NTPH acid are provided in Table 2 and in Figures 5 and 6.

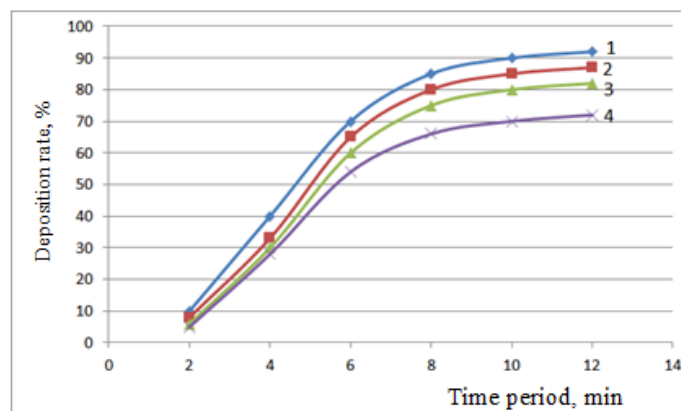
**Table 2**

The results of fine purification of electrolyte from Fe<sup>+3</sup> with the help of NTPH acid

pH	Fe initial, g/dm <sup>3</sup>	NTPH consumption, g/dm <sup>3</sup>	Fe <sup>+3</sup> residual, mg/dm <sup>3</sup>	Precipitation mass Fe <sub>3</sub> (NTPH) <sub>2</sub>	Iron recovery, %
3.0	1.2	2.6	0.6	15.49	99.9
3.2	1.5	3.3	1.2	19.93	99.8
3.5	1.8	3.9	7.4	23.16	99.6
3.8	2.0	4.4	10.3	26.57	99.5

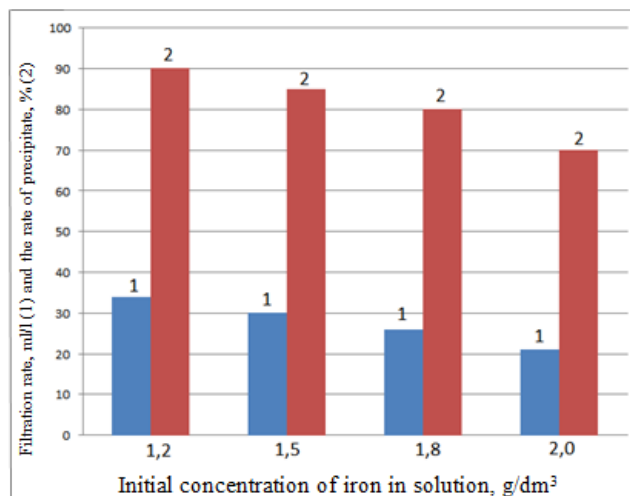


**Fig. 5.** Change of free filtration rate during the period of time at different initial concentrations of iron ions in the solution  $\text{g/dm}^3 \text{Fe}^{3+}$ : 1.2; 2-1.5; 3-1.8; 4-2.0



**Fig. 6.** The change of free deposition rate during certain time period and at different initial concentrations of iron ions in solution  $\text{g/dm}^3 \text{Fe}^{3+}$ : 1- 1.2; 2-1.5; 3-1.8; 4-2.0

Assessment of final rates of filtration and precipitate deposition depending on initial concentration of iron in solution is presented in Figure 7. Analyzing the obtained diagrams, it can be concluded that initial iron concentration influence considerably the filtration of produced precipitates: the highest filtration rate and maximal rate of precipitate deposition is observed when initial iron concentration is minimal.



**Fig. 7.** Dependence of filtration rate and the rate of precipitate deposition on initial concentration of iron ions in solution

Thus, it has been found out that new reagent- precipitator, complexon of nitrile-trimethylene-phosphonic acid (NTPh) provides advanced purification of electrolyte from iron ions up to 0.6-10 mg/dm<sup>3</sup>. Clearance depth and rheological properties of pulp depend on initial iron concentration in purified solution: the less initial concentration is the more effective, deeper and faster the process of precipitates formation is, and the better rheological properties are.

The results of comparative experiments showed that average deposition rate of the formed precipitate Fe<sub>2</sub>(NTPh)<sub>3</sub> is 8.8 times higher than the deposition rate of hydroxide precipitate Fe(OH)<sub>3</sub>, that have been formed before. Besides average rate of pulp filtration rate Fe<sub>2</sub>(NTPh)<sub>3</sub> is 15 times higher than filtration rate of hydroxide pulp Fe(OH)<sub>3</sub>. It has been defined that the formed precipitate can be used after drying at the enterprises of ferrous metallurgy for the production of valuable iron-phosphoric alloy.

#### 4.4. Cementation purification of solution from copper ions

The process of impurities cementation from zinc sulphate solution with metal zinc is based on electrochemical reaction:  $Me^{2+} + Zn \rightarrow Me + Zn^{2+}$ . Besides impurity metal converts from ionic condition into metal state, and zinc converts from metal state into ionic condition. Cementation reaction goes on in the case when it goes along with reduction of thermodynamic isobaric potential. It occurs if displaced metal possesses more positive electrochemical potential than zinc does.

If zinc is abundant the cementation process will proceed until there is the balance defined by equality of isobaric potentials or by equality of electrochemical reversible potentials (that is the same) of both metals. Table 3 provides results of cementation purification of electrolyte from copper.

**Table 3**

Indicators of electrolyte cementation purification from copper

Initial concentration of copper, mg/dm <sup>3</sup>	Final concentration of copper, mg/dm <sup>3</sup>	Zinc consumption stoich. mg/dm <sup>3</sup>	Zinc consumption per 50 dm <sup>3</sup> , g	Excess coefficient, %	Zinc consumption per 50 dm <sup>3</sup>	Change of zinc, from 120 g/dm <sup>3</sup> +
150	0.3	152.10	7.61	200	15.22	0.213
120	0.3	121.55	6.08	200	12.16	0.172
100	0.2	101.40	5.07	150	7.60	0.132
75	0.2	75.42	3.77	150	5.66	0.098
50	0.1	50.70	2.53	150	3.79	0.066

It follows from the represented results that residual copper concentration in solution after cementation is 0.1-0.3 mg/dm<sup>3</sup>. This corresponds to practical indicators of operating zinc plants. Consumption of zinc dust for advance purification of electrolyte (50 dm<sup>3</sup>) is not more than 15 g that should have positive effect on profitability operation. Increase of zinc concentration in electrolyte by analytic method couldn't have been defined. Comparing with 120 g/dm<sup>3</sup> of zinc change on 200 mg by titrating is not fixed. The result was obtained by calculating method taking into account secondary reaction of solving powder.

## 5. Conclusions

As reserves of ore raw materials are depleted in Kazakhstan there is the necessity to involve low-grade mineral and technogenic raw materials into the process of metallurgic processing. The use of technogenic raw materials is always connected with formation of great amount of unknown technologic products – production wastes that require not only development of new approaches to working with them but also increase ecological load on the environment. The peculiarity of transition to the new types of resources is development of new technological procedures taking into account the changed composition of raw material, going along with technical modernization of operating metallurgic complexes, and formation of technological solutions that differ by increased content of impurities and analysis of other aspects.

In Kazakhstan as well as in China (Kinnunen and Kaksonen, 2019) and in some other countries nowadays there is a big gap between the development levels of national and foreign metallurgic enterprises, where international economy is developed in such aspects as technologies, complex indicators of resources usage and wastes management. This circumstance directly causes considerable share of ineffective consumption of resources, considerable emissions of greenhouse gases, sulphur oxides (SO<sub>x</sub>), dust and others.

As the quality of primary ores becomes worse, mining industry have to recover metals from more complicated ores. Semi-products, current tails, and other technogenic objects can become technically and economically competitive variant as the source of raw material and new types of products. Part of metals contained



in raw feedstock haven't been recovered as there is neither technology nor demand for them. The results of given research can have commercial perspectives for usage when wastes and low-grade ores are processed. But these results should be registered as process procedure. Under conditions of changing market demands and trends the technologies are improved and additional recovery of precious associated components resulted in production of new products is of scientific and practical interest.

Experimental data showed that there is increased number of  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  ions in sulphate solutions produced in leaching of low-grade zinc raw material. In order to achieve the required permissible concentrations of the mentioned impurities it is required to include the following operations into the processing procedure: deposition of  $\text{Fe}^{+3}$  ions present in the solution, electrochemical oxidation of  $\text{Fe}^{+3}$  ions, advance purification of the solution from iron with the help of complexon - nitrile-trimethylene-phosphonic acid (NTPh), cementation purification of solution from copper ions. The formed precipitate of iron complexonate (after drying) can be used as a semi-product at the enterprises of ferrous metallurgy for production of valuable iron-phosphoric alloy.

The results obtained at the given stage can be of economic and industrial interest for hydrometallurgical production of non-ferrous, rare, and disseminated metals of Kazakhstan, Russia, and other countries. These countries are currently engaged in problems of processing of low-grade feedstock containing precious components. However, up-to-date technologies are oriented only on base metals such as Ni, Zn or Cu, and remaining part of the material is left unused. Development of new effective approaches to hydrometallurgical processing of low-grade mineral and technogenic raw materials of Kazakhstan will enable considerably to reduce amount of mined raw materials due to involving accumulated technogenic materials, to decrease ecological burden on the environment, to increase complexity of mineral raw materials use. Besides this will create prerequisites for the development of circular economy with an emphasis on wastes management and valorization of enterprises resources.

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