

Article

Development of Technology for Processing Pyrite–Cobalt Concentrates to Obtain Pigments of the Composition Fe_2O_3 and Fe_3O_4

Tatyana Chepushtanova ¹, Aliya Altmyshbayeva ^{1,*}, Yerik Merkibayev ¹, Kulzira Mamyrbayeva ¹, Zhanat Yespenova ¹ and Brajendra Mishra ²

- ¹ Metallurgy and Mineral Processing Department, Satbayev University, Almaty 050013, Kazakhstan; t.chepushtanova@satbayev.university (T.C.); y.merkibayev@satbayev.university (Y.M.); k.mamyrbayeva@satbayev.university (K.M.); 900722400595-d@stud.satbayev.university (Z.Y.)
- ² Mechanical & Materials Engineering Department, Worcester Polytechnic Institute, Worcester, MA 01609-2280, USA; bmishra@wpi.edu
- * Correspondence: a.altmyshbayeva@satbayev.university

Abstract

This paper presents the results of a study on the development of a processing technology for pyrite–cobalt concentrates to obtain iron oxide pigments (Fe_2O_3 and Fe_3O_4) via high-temperature hydrolysis. It was found that, in a single operation, the concentrate can be effectively purified from lead, zinc, and copper, yielding an iron–nickel–cobalt product suitable for further processing by standard technologies, such as smelting into ferronickel. The scientific originality of research concludes in a mechanism of stepwise selective chloride volatilization, which was established as follows: stage I (500–650 °C)—removal of lead; stage II (700–750 °C)—chlorination of copper and iron; stage III (850–900 °C)—volatilization of nickel and cobalt. Microprobe analysis of the powders obtained from high-temperature hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ revealed the resulting Fe_3O_4 and Fe_2O_3 powders with particle sizes 50 μm and 100 μm . A visual color palette was created, corresponding to different $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ ratios in the pigment composition—ranging from black (magnetite) to red (hematite)—and potential application areas. For the first time, the new technological scheme was proposed of pigments Fe_2O_3 and Fe_3O_4 production from pyrite–cobalt concentrates via combination of oxidized roasting with subsequent chlorination and high-temperature hydrolysis of the products.

Keywords: pyrite–cobalt concentrate; crystallization; high-temperature hydrolysis; microdispersed and nanodispersed powders; iron oxide pigments; hematite; magnetite



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1. Introduction

Pyrite or pyrite–cobalt concentrates represent a valuable raw material for the production of sulfuric acid, metallic iron, elemental sulfur, gold, and a range of non-ferrous metals such as nickel and cobalt [1–3]. In recent years, the processing of pyrite concentrates has gained increasing relevance due to several key factors.

Waste accumulation issues: At many processing plants, pyrite concentrate obtained via flotation enrichment is not further processed but rather stockpiled, leading to the formation of environmentally hazardous tailing storage facilities containing heavy metals and sulfur. This results in soil and water contamination, the release of sulfur dioxide during oxidation,

and even spontaneous combustion. Processing pyrite is also a means of remediating such waste [4,5].

Recovery of associated valuable components: Amid global ore depletion and declining metal grades, flotation tailings containing pyrite and various non-ferrous metals are becoming an alternative source for metal recovery. Pyrite concentrates often contain economically significant amounts of gold, copper, zinc, nickel, and cobalt. Integrated processing enables more efficient utilization of mineral resources and improves the profitability of production [6–8].

Advances in processing technologies: The most relevant and in-demand technologies include modern methods such as activation roasting, pyrolysis, high-temperature chlorination, bacterial leaching, and autoclave leaching [9,10]. These approaches significantly enhance the efficiency, sustainability, and environmental compatibility of pyrite processing, aligning with the goals of sustainable development.

The significance of this trend is also reflected in the global export volumes of pyrite concentrates, as illustrated in Figure 1 [11].

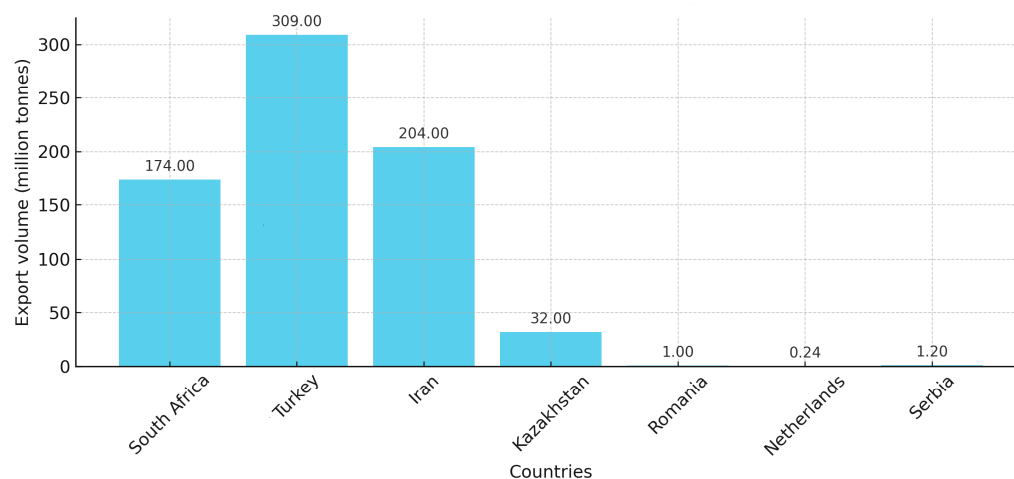


Figure 1. Export volumes of pyrite concentrates by country (in million tonnes).

The critical group of metals that can be extracted from pyritic feedstocks includes those classified as strategically important for most countries, particularly nickel, cobalt, and iron-containing products [12–16].

Currently, a variety of technologies are available for processing pyrite and pyrite–cobalt feedstocks. For instance, the Polymetal plant in Russia utilizes flotation and subsequent hydrometallurgical methods for pyrite concentrate processing, enabling the recovery of gold [17].

Glencore, one of the world’s largest metallurgical companies, utilizes sulfuric-acid-based technologies for processing pyritic feedstocks. For example, in North America (Canada and the United States), the company employs pyrometallurgical methods for pyrite concentrate treatment, including sulfuric acid production. The process involves roasting of pyrite concentrates to generate sulfur dioxide, which is subsequently converted into sulfuric acid. This method enables the efficient processing of large volumes of pyrite material [18].

The Cerro Verde plant in Peru is among the largest facilities processing copper–gold–pyrite ores. It applies pyrometallurgical and flotation methods to recover copper and pyrite concentrates, with sulfuric acid produced as a by-product.

In China, the Shaanxi Nonferrous Metals plant actively implements biomining technologies (bioleaching) to process complex pyritic ores, including pyrite concentrates containing gold and copper.

BHP Billiton in Australia uses conventional methods for processing pyrite concentrates, such as pyrometallurgy and sulfuric-acid-based leaching, to recover copper, gold, and sulfur [19–21].

Recent research and development efforts in the field of pyrite concentrate processing are focused on improving the efficiency of valuable metal extraction while minimizing environmental risks. Innovative approaches—such as integrated processing using advanced chemical reagents and technologies—open new possibilities for the treatment of pyrite cinders and concentrates [22,23].

Pyrite cinders, a by-product of roasting pyrite concentrates, are currently being processed using advanced technologies and serve as a source for the recovery of various metals and sulfuric acid. They also act as a source of iron for fertilizers—in the form of Fe_2O_3 or FeSO_4 derived from the cinders—which are used to treat iron-deficient soils. In Russia, over 250 million tonnes of pyrite cinders have accumulated to date, with approximately 5 million tonnes added annually. In Kazakhstan, an estimated 170 million tonnes of pyrite cinders of various origins are stockpiled [22,24].

At present, pyrite cinders are partially used as additives in the production of cement, glass, refractory materials, copper-bearing pig iron, and other industrial applications. The presence of valuable components in the cinders, such as iron oxides, noble metals, non- and ferrous and rare metals (Co, Ni, Ga, Ge, In, Tl, Se, and Te), is currently utilized inefficiently and does not address the issues of comprehensive raw material processing [23,25]. Although the content of rare metals ranges from 0.001 to 0.5%, they become economically significant when subjected to integrated processing.

A new generation of autoclave processing technologies has emerged, enabling the comprehensive recovery of valuable components from pyrite-based materials. These technologies involve high-pressure oxidative leaching in chloride media (e.g., NaCl and CaCl_2) at temperatures between 110 and 210 °C and pressures up to 20 atm, followed by selective precipitation of iron as hematite or its conversion into high-purity pigments. Subsequent recovery of base, precious, and rare metals is achieved via sorption and electrolysis techniques [26].

The most common synthesis methods for Fe_3O_4 have been examined. Table 1 provides a comparative analysis of different synthesis routes for iron oxide powders [27,28].

Table 1. Comparative analysis of synthesis methods for iron oxide pigments.

Synthesis Method	Applications	Advantages	Limitations
Co-precipitation	Fe_3O_4 , Fe_2O_3	Simplicity, low cost	Limited control over particle size
Hydrothermal	Fe_3O_4 , Fe_2O_3	Morphology control, high crystallinity	Requires high temperature and pressure
Biosynthesis	Fe_3O_4	Eco-friendliness, safety	Scale-up complexity
Green synthesis methods	Fe_3O_4 , Fe_2O_3	Eco-friendliness, use of renewable resources	Possible impurities, limited control over properties
Patented methods	Fe_3O_4 , Fe_2O_3	Innovation, enhanced pigment properties	Limited access, potential licensing restrictions

China is currently the global leader in pigment demand. Market volume: It is projected that, by 2035, the global market for iron oxide pigments will reach 682 thousand tonnes,

with an estimated value of USD 934 million. Growth rate: The expected compound annual growth rate (CAGR) is approximately 1.5% in volume and 3.0% in value. Growth drivers: rapid development in the construction sector, ongoing urbanization, and large-scale infrastructure projects are key factors driving the increasing demand for iron oxide pigments [29].

The global market for Fe_3O_4 and Fe_2O_3 pigments continues to demonstrate steady growth, driven by the expansion of the construction industry, increasing production of coatings and plastics, and the adoption of environmentally sustainable technologies. Asia—particularly China and India—leads in terms of consumption volume, while Europe and North America focus on sustainability and innovation. Emerging regions such as South America, the Middle East, and Africa represent promising markets with strong growth potential in the coming years [29].

In addition to metals, pyrite cinders typically contain an aluminosilicate component (25–30%), which, after separation and washing, can be used for technical glass production.

Innovative technologies for comprehensive pyrite cinder processing have been developed at Tomsk Polytechnic University (Russia). Their method enables the recovery of gold, silver, copper, zinc, iron, and other metals. The process includes drying, roasting, and sintering with ammonium chloride, which allows effective separation of the elements [22,23,25].

In Japan, a method combining cyanidation and chloride processing has been proposed for the recovery of gold and silver and the concentration of iron in magnetic separation products. It has been shown that the chloride–chlorination process is preferable due to its higher metal recovery efficiency, reduced environmental impact, and the potential for diversified applications of the iron-containing products in ferrous metallurgy and cement production.

Elemental sulfur is industrially extracted from pyrite at several plants in Finland, Sweden, Spain, and other countries. Sulfur can be recovered by thermal decomposition of pyrite concentrate in a non-oxidizing atmosphere [30].

A novel chemical method for iron production from low-grade ores has been developed based on the Fe–Cl thermochemical cycle. The process includes roasting in a reducing atmosphere, HCl leaching to form FeCl_2 , crystallization of iron chloride, followed by low-temperature pyrohydrolysis (120–800 °C) to regenerate HCl and produce iron oxide, which is then refined via hydrogen reduction to >99 % pure iron in a closed-loop system with HCl reuse. Similar chlorination-based approaches have also been explored for titanium extraction from ilmenite using chlorinating agents such as carbon tetrachloride [31].

In the United States, a high-temperature hydrolysis process has been developed for ferric chloride solutions, yielding ultra-pure iron oxides and enabling hydrochloric acid regeneration. A major advantage of this processing method, as noted in all studies, is the complete removal of sulfur from the iron-containing solutions [32–34].

According to operational experience at the Sherritt Gordon Mines plant in Fort Saskatchewan, Canada, ammoniacal leaching has proven to be economically viable for the processing of intermediate metallurgical products that are sufficiently rich in nickel. Nickel and cobalt are precipitated in autoclaves using hydrogen. Ammonium sulfate is subsequently recovered from the spent solution via crystallization and used as a chemical fertilizer in agriculture. The overall metal recovery rates achieved using this method are approximately 90% for nickel, 45% for cobalt, 89% for copper, and 75% for sulfur [26,35].

Another existing approach involves autoclave hydrogen sulfide leaching of copper–nickel mattes and anodic slimes from nickel electrorefining processes. In general, hydrometallurgical schemes offer comprehensive processing of ores, concentrates, and intermediate

industrial products. However, their major drawbacks are the multi-stage nature of the processes and the complexity of the required equipment [26,35].

The reviewed literature indicates that, to date, no highly efficient integrated technology has been developed for processing nickel–cobalt–iron-containing materials [22,25,33,36].

One promising direction for improving metal recovery from ores and concentrates lies in the use of alkaline reagents in metallurgical processes. Among them, sodium carbonate is widely used in non-ferrous metallurgy [35].

Chlorination technology is also widely applied in the field of non-ferrous metallurgy. The high reactivity of chlorine and the strong chemical interactions of metal chlorides with other compounds ensure efficient recovery of valuable components from processed materials, such as cobalt–pyrite concentrates [25,33].

A key research focus involves the development of electrochemical oxidation methods for sulfides, aiming to transfer non-ferrous metals into solution followed by selective extraction via various separation techniques. Sodium-chloride-based electrolytes are considered among the most promising solvents for electrochemical leaching of sulfide-based nickel–cobalt materials [22,33,37].

Studies on the chlorination of pure compounds of nickel, cobalt, and iron have shown that chlorination of nickel and cobalt sulfides begins at approximately 100 °C and is nearly complete at 550–600 °C. Therefore, gas-phase chlorination with chlorine and its compounds proves highly effective for processing various types of non-ferrous metal-bearing materials [34,38].

Pre-reduction of the feed or the addition of reducing agents during chlorination, as well as the inclusion of sulfides in the charge, significantly enhances the process. Many researchers have noted increased efficiency and lower chlorination temperatures for metal oxides when reducing agents are used [38,39].

The authors of this study have demonstrated the feasibility of using chloride volatilization to process pyrite cinders and polymetallic industrial products from beneficiation plants. Chlorinating roasting is proposed to be carried out in a fluidized bed at relatively low temperatures [23,25,39].

Of particular interest is the industrial-scale implementation of a chloride volatilization process applied to pellets made from high-quality pyrite cinders at the Kowa Seiko plant in Tobata, Japan [23,25].

Pyrite–cobalt concentrates are also a promising feedstock for producing value-added products such as nanomaterials and pigments [25,36].

Iron oxide pigments, including Fe_3O_4 and Fe_2O_3 , are widely used in various industries due to their magnetic, optical, and chemical properties. Contemporary synthesis methods focus on producing nanostructured forms with controlled characteristics [40–44].

The proposed hydrochloric-acid-based processing technology for pyrite–cobalt concentrates—targeting the production of pigments and ferrites with hydrochloric acid regeneration in the vapor–gas phase—addresses this challenge. It offers economic viability by reducing the complexity of process equipment and improving operational efficiency [23,25,33,39].

The main aim of this research and the main idea are to develop a technology for processing pyrite–cobalt concentrate by combining chloride sublimation and high-temperature hydrolysis methods to obtain ultrafine powders of Fe_3O_4 and Fe_2O_3 and pigments based on them. Such combination of the process is used for the first time for classical pyrite–cobalt-bearing concentrate treatment.

2. Materials and Methods

The initial material used in this study consisted of samples obtained from oxidative roasting of a sulfide concentrate—an intermediate product formed during the processing of cobalt–pyrite concentrates at the Sokolov–Sarbai Mining and Processing Production Association JSC (Kokshetau, Kazakhstan).

The chemical composition of the concentrate was as follows: iron—8.68%; nickel—15.0%; cobalt—24.0%; copper—11.78%; zinc—6.01%; and lead—16.4%, Table 2, Figure 2. According to mineralogical analysis, the oxide phases present in the concentrate included Fe_2O_3 , Ni_2O_3 , Co_2O_3 , Cu_2O , ZnO , and PbO .

Table 2. Chemical composition of the Sokolov–Sarbai Mining concentrate.

Element	Oxide	Element wt%	Oxide Molar Mass	Element Atomic Mass	Element Count	Element wt in Oxide	Element Fraction in Oxide	Mineralogical wt%
Fe	Fe_2O_3	8.68	159.69	55.85	2	111.7	0.6995	12.41
Ni	Ni_2O_3	15.0	165.38	58.69	2	117.38	0.7098	21.13
Co	Co_2O_3	24.0	165.87	58.93	2	117.86	0.7106	33.78
Cu	Cu_2O	11.78	143.09	63.55	2	127.1	0.8883	13.26
Zn	ZnO	6.01	81.38	65.38	1	65.38	0.8034	7.48
Pb	PbO	16.4	223.2	207.2	1	207.2	0.9283	17.67

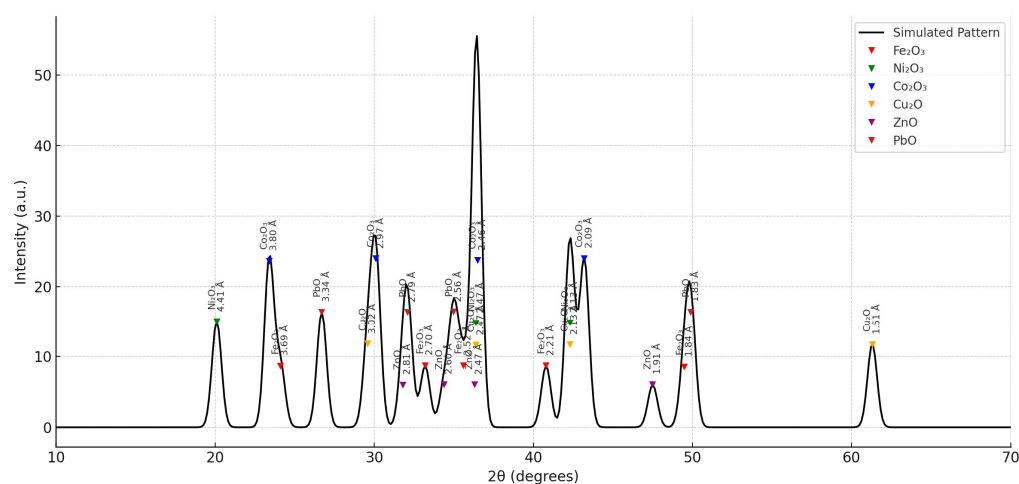


Figure 2. XRD analysis of initial Sokolov–Sarbai Mining concentrate.

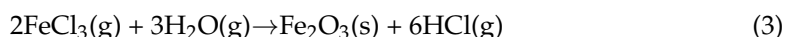
The aim of this part of the study was to investigate the chloride volatilization process in order to concentrate iron, nickel, and cobalt in the roasted residue, while volatilizing copper, zinc, and lead. The study also sought to evaluate the extent of volatilization of these non-ferrous metals.

2.1. Experimental Procedure for the Chloride Volatilization Process

Chlorination of the charge was carried out in the presence of a steam–air mixture, since the degree of chlorination of iron oxides decreases proportionally with the oxygen and water vapor content in the gas phase due to hydrolysis of iron chlorides. The role of the reducing agent (charcoal) is to facilitate the displacement of oxygen from the oxide by chlorine, which is generated from the decomposition of calcium chloride. The released oxygen reacts with carbon, thereby shifting the equilibrium toward the formation of metal chlorides. The addition of sulfide compounds enhances the chloride volatilization process by forming disulfur dichloride (S_2Cl_2), a highly effective chlorinating agent.

In these experiments, calcium chloride (CaCl_2) was used as the chlorinating reagent for the target oxide mixture. This choice was due to its ability to decompose almost completely in the presence of furnace gases (SO_2 and O_2), releasing elemental chlorine and forming calcium sulfide as a by-product.

To better illustrate the mechanism, the following reactions are proposed:



These reactions support the role of calcium chloride as a chlorinating agent and explain the influence of reducing conditions and water vapor on the efficiency of selective chlorination.

The experiments were conducted at temperatures ranging from 1000 to 1150 °C in the presence of a reducing agent and a steam–air mixture. Activated charcoal was used as the reducing agent. The thoroughly ground charge was placed in a corundum crucible (Lanzhou Dahong Engineering Co., Lanzhou, China), which was then inserted into a quartz ampoule positioned in the working zone of a vertical shaft electric furnace (Lonroy, Hubei, China). Quartz and corundum tubes were introduced into the ampoule for supplying the steam–air mixture and removing exhaust gases.

Air was delivered using a micro-compressor (KNF Neuberger, Salzweiler, Germany). The furnace temperature was measured using a chromel–alumel thermocouple (Wuhan Global Metal Engineering Co, Wuhan, China) connected to a potentiometer. To capture gaseous products from the chloride volatilization process, absorption flasks (Pavlovsk Glass Factory, Moscow, Russia) with Raschig rings were installed.

Chlorination of the charge was performed at a given temperature for 1 h. In all experiments, the sample mass of the oxide mixture was 1.0 g. The roasted residues obtained after chloride volatilization were analyzed for iron (Fe), nickel (Ni), cobalt (Co), copper (Cu), lead (Pb), and zinc (Zn). The experimental setup is illustrated in Figure 3.

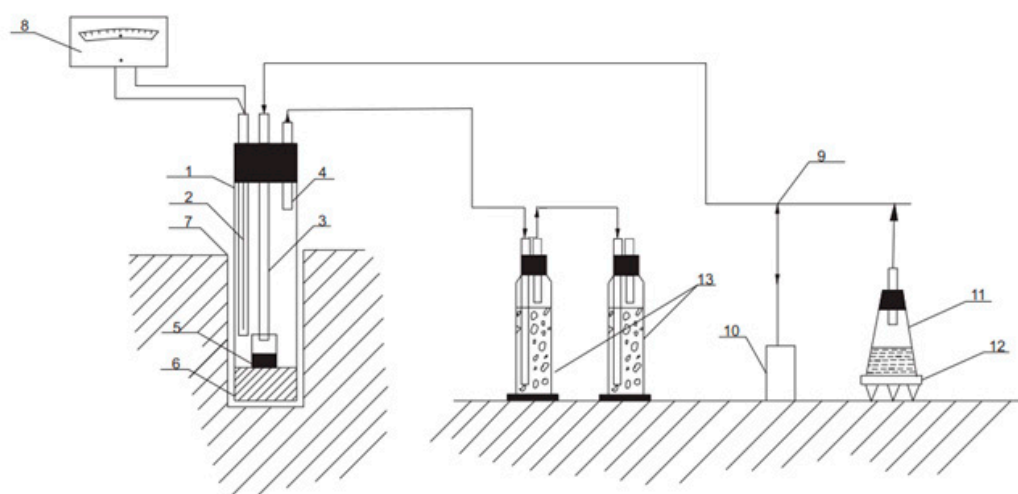


Figure 3. Schematic diagram of the setup for high-temperature chlorinating roasting. 1—quartz ampoule with stopper; 2—thermocouple in a quartz sheath; 3—corundum tube for steam–air mixture supply; 4—quartz tube for gas outlet; 5—corundum crucible containing the test charge; 6—lightweight chamotte crucible support; 7—vertical shaft electric furnace; 8—millivoltmeter; 9—three-way valve; 10—micro-compressor for air supply; 11—water flask; 12—electric heating plate; 13—absorption flasks with Raschig rings.

The residues obtained after chloride volatilization were analyzed for Fe, Ni, Co, Cu, Pb, and Zn content using an X-ray diffractometer (XRD) D8 Advance (Bruker AXS GmbH, Karlsruhe, Germany) equipped with a CuK α radiation source, operating at 40 kV and 40 mA. Diffraction data processing and calculation of interplanar spacings were carried out using EVA software (version DIFFRAC.EVA, Bruker AXS GmbH, Karlsruhe, Germany).

Phase identification and interpretation of the diffraction patterns were performed using the Search/Match function with the PDF-2 powder diffraction database, enabling the determination of the relative proportions of crystalline phases. The microstructure of the solid samples was examined via scanning electron microscopy SEM-JSM-IT300 (JEOL Ltd., Tokyo, Japan).

To determine the elemental composition of the original concentrates and residues, X-ray fluorescence (XRF) analysis was used. Semi-quantitative elemental analysis was performed on a wavelength-dispersive X-ray fluorescence spectrometer (Axios 1 kW, PANalytical, Almelo, The Netherlands). The data were processed using SuperQ software (version 6, PANalytical, Almelo, The Netherlands) and the Omnian 37 software package, based on the Fundamental Parameters (FP) model. The results provided a qualitative and semi-quantitative elemental profile of the samples.

The drying and calcination of iron oxide powders were carried out in a fixed bed using an electric furnace (Zhengzhou Brother Furnace Co., Ltd., Zhengzhou, China, model BR-17AM-5) under a reduced pressure of -0.05 MPa. The experimental setup is shown in Figure 2. The residence time of the sample in the furnace ranged from 15 to 60 min, and the temperature was varied between 400 and 1100 °C. After thermal decomposition, the weight loss of the samples was monitored, and the contents of iron and sulfur in the treated product were determined.

2.2. Thermodynamic Analysis of the Chloride Volatilization Process

Thermodynamic analysis of the chloride volatilization behavior of cobalt, nickel, iron, copper, zinc, and lead compounds indicates that, under specific conditions, lead, zinc, and copper can be volatilized in the form of chlorides, while iron, nickel, and cobalt remain in the residue.

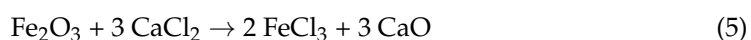
In this study, the thermodynamics of the key reactions involved in the chloride volatilization process were evaluated using the HSC Chemistry software, version 5, Metso Finland Oy, Espoo, Finland. The results of the thermodynamic calculations are summarized in Table 3.

For all the examined reactions, ΔG decreases with increasing temperature, indicating that the thermodynamic favorability of chloride volatilization improves at higher temperatures. This is characteristic of reactions with positive entropy change ($\Delta S > 0$), where the increase in temperature enhances the $-T\Delta S$ term, thus reducing ΔG .

A comparison of the thermodynamic parameters for the selected reactions is summarized below:



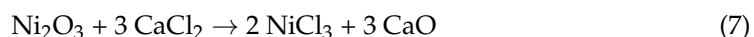
ΔG approaches zero at 700 °C and becomes negative at 800 °C, indicating favorable conditions. The logK value reaches 2.13 at 1100 °C, suggesting a high degree of reaction completeness. This reaction proceeds efficiently within the medium-temperature range.



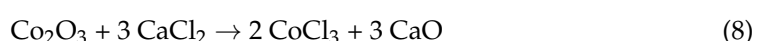
This is similar in behavior to the copper reaction but initiates slightly later ($\Delta G < 0$ from 700 °C). The logK value reaches 2.23 at 1100 °C, also indicating a high extent of conversion.



This reaction is the most thermodynamically favorable, with $\Delta G < 0$ starting at 600 °C. The logK is already 0.44 at 600 °C and increases to 2.18 by 1100 °C. This suggests that lead is among the first elements to be volatilized upon heating.



Thermodynamic favorability is limited at lower temperatures ($\Delta G > 0$ until 800 °C), with the reaction becoming effective only from 900 °C, where $\log K > 0$. At 1100 °C, $\log K = 1.51$, which is acceptable but lower than for Fe and Pb.



The behavior is similar to that of the nickel reaction; ΔG becomes negative only from 900 °C. The logK value reaches 1.44 at 1100 °C, indicating reasonable conversion but requiring elevated temperatures.

In all cases, ΔS is positive (100–160 J/mol·K), making these reactions increasingly favorable with rising temperature. The highest entropy contributions are observed for the Ni and Co reactions; however, these reactions also exhibit high initial ΔG values, necessitating higher temperatures to proceed efficiently.

Table 3. Thermodynamic parameters of the main reactions in the chloride volatilization process.

Reaction	T (°C)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol·K)	K	logK
$\text{Cu}_2\text{O} + \text{CaCl}_2 \rightarrow 2 \text{CuCl}_2 + \text{CaO}$	600	150	19.03	150	0.0727	−1.14
	700	150	4.03	150	0.6079	−0.22
	800	150	−10.97	150	3.4206	0.53
	900	150	−25.97	150	14.3374	1.16
	1000	150	−40.97	150	47.9817	1.68
	1100	150	−55.97	150	134.6702	2.13
$\text{Fe}_2\text{O}_3 + 3 \text{CaCl}_2 \rightarrow 2 \text{FeCl}_2 + 3 \text{CaO}$	600	120	6.49	130	0.4090	−0.39
	700	120	−6.51	130	2.2357	0.35
	800	120	−19.51	130	8.9052	0.95
	900	120	−32.51	130	28.0247	1.45
	1000	120	−45.51	130	73.6590	1.87
	1100	120	−58.51	130	168.1831	2.23
$\text{PbO} + \text{CaCl}_2 \rightarrow \text{PbCl}_2 + \text{CaO}$	600	80	−7.32	100	2.7392	0.44
	700	80	−17.32	100	8.5002	0.93
	800	80	−27.32	100	21.3590	1.33
	900	80	−37.32	100	45.8685	1.66
	1000	80	−47.32	100	87.3583	1.94
	1100	80	−57.32	100	151.4753	2.18
$\text{Ni}_2\text{O}_3 + 3 \text{CaCl}_2 \rightarrow 2 \text{NiCl}_3 + 3 \text{CaO}$	600	180	40.30	160	0.0039	−2.41
	700	180	24.30	160	0.0496	−1.30
	800	180	8.30	160	0.3946	−0.40
	900	180	−7.70	160	2.2031	0.34
	1000	180	−23.70	160	9.3877	0.97
	1100	180	−39.70	160	32.3888	1.51
$\text{Co}_2\text{O}_3 + 3 \text{CaCl}_2 \rightarrow 2 \text{CoCl}_3 + 3 \text{CaO}$	600	175	39.66	155	0.0042	−2.37
	700	175	24.16	155	0.0505	−1.30
	800	175	8.66	155	0.3788	−0.42
	900	175	−6.84	155	2.0160	0.30
	1000	175	−22.34	155	8.2513	0.92
	1100	175	−37.84	155	27.5055	1.44

To further analyze the chloride volatilization process, phase diagrams for the Fe–Cl–O system were generated using HSC Chemistry at 800 and 1000 °C, as shown in Figure 4.

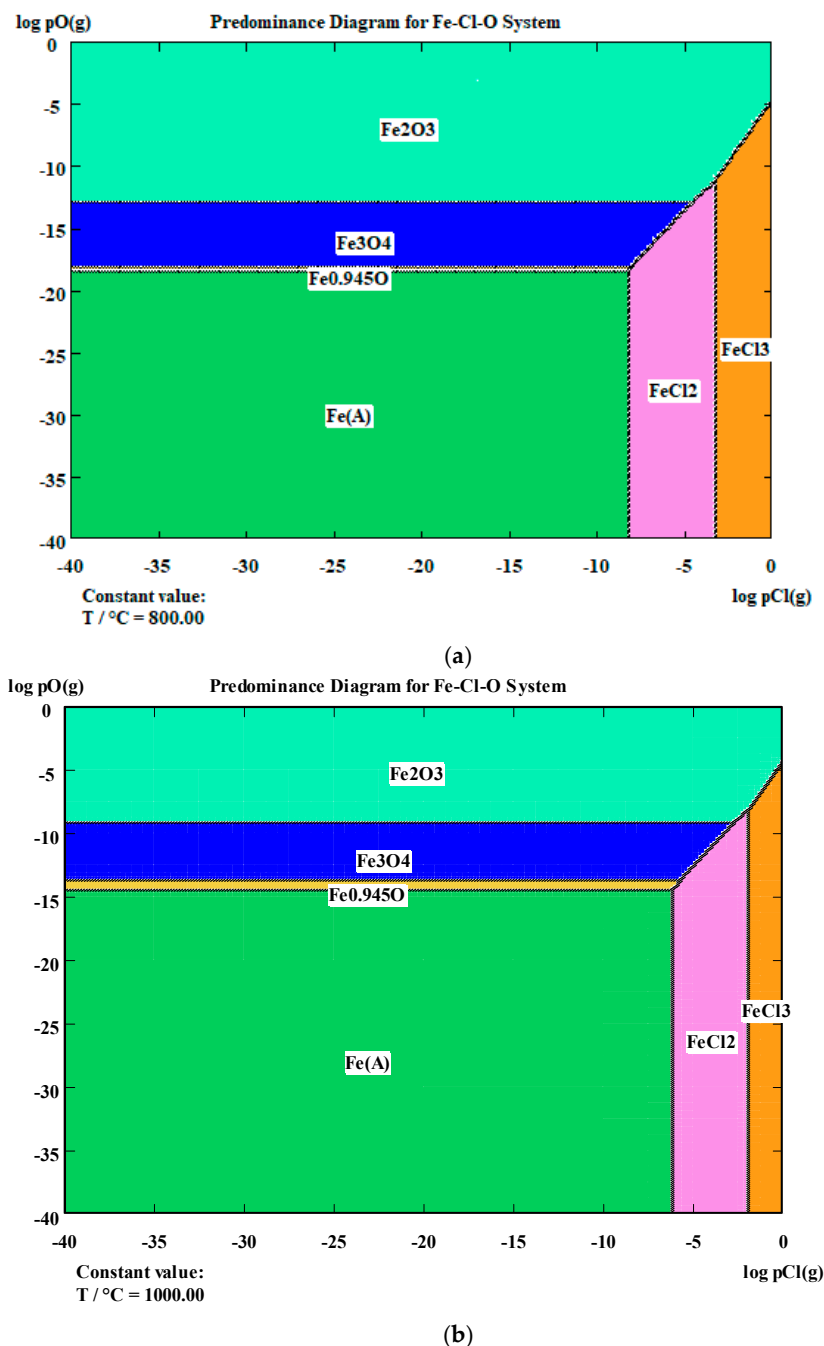


Figure 4. Phase diagrams of the Fe-Cl-O system at 800 and 1000 °C. (a) Fe-Cl-O system at 800 °C; (b) Fe-Cl-O system at 1000 °C.

At 800 °C, the Fe-Cl-O system is dominated by the solid phases Fe_2O_3 , Fe_3O_4 , and $FeCl_2$. The gaseous form of $FeCl_3$ is unstable under conditions of low chlorine partial pressure (pCl_2) or chlorine deficiency. The formation of volatile chlorides at this temperature is therefore limited.

At 1000 °C, the stability of gaseous $FeCl_3$ increases with temperature. Under high chlorine potential (high pCl_2), the system favors transitions from oxides to volatile chlorides. The diagram indicates the following sequence of transformations with increasing chlorine potential: $FeO \rightarrow FeCl_2 \rightarrow FeCl_3$.

Thus, under chloride volatilization conditions, a temperature of 1000 °C enables the conversion of iron into its volatile chloride form. However, under moderate conditions, solid oxides and chlorides remain predominant.

Analysis of equilibrium phase diagrams for the Ni-Cl-O, Co-Cl-O, Zn-Cl-O, and Ca-Cl-O systems also provides insight into optimal thermodynamic conditions for selective volatilization, as summarized in Table 4.

Table 4. Analysis of equilibrium phase diagrams of Ni-Cl-O, Co-Cl-O, and Ca-Cl-O systems.

System	Optimum T for Chloride Sublimation	Volatile Forms	Conditions for Gas Formation
Ni-Cl-O	1000 °C	NiCl ₃ (r)	High pCl ₂
Co-Cl-O	1000 °C	CoCl ₃ (r)	High pCl ₂
Fe-Cl-O	1000 °C	FeCl ₃ (r)	Moderately high pCl ₂
Zn-Cl-O	900–1000 °C	ZnCl ₂ (g)	Moderate pCl ₂ , presence of CaCl ₂
Ca-Cl-O	Not required	No	CaCl ₂ is stable in the liquid phase

Based on the thermodynamic analysis, the relative feasibility of chloride volatilization for different metals in the temperature range 600–1000 °C can be ranked as follows: Volatilization Priority: Pb > Cu ≈ Fe > Co ≈ Ni. Remarks: lead is the easiest to volatilize; cobalt and nickel require high temperatures for volatilization.

Based on the obtained data, graphs were constructed to illustrate the dependence of ΔG and $\log K$ on temperature for each reaction, as shown in Figure 5.

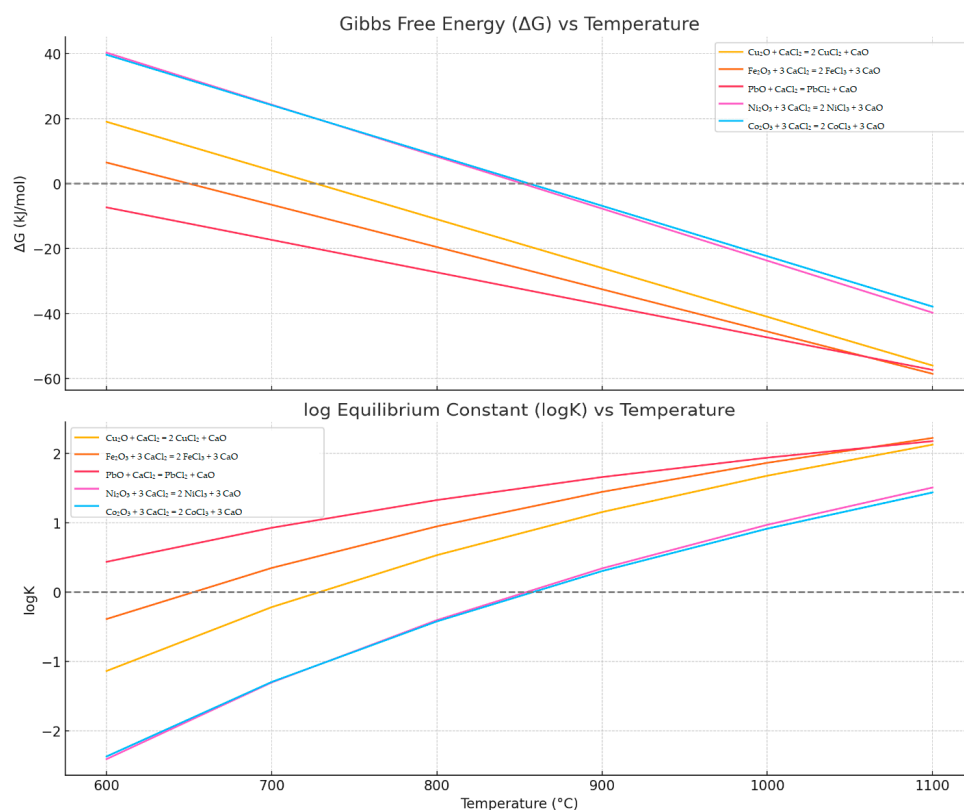


Figure 5. Temperature dependence of ΔG and $\log K$ for chloride volatilization reactions.

These plots demonstrate the ΔG vs. temperature relationships, which indicate the temperature at which each reaction becomes thermodynamically favorable ($\Delta G < 0$), and the $\log K$ vs. temperature relationships, which reflect the extent to which the equilibrium is shifted toward the products ($\log K > 0$).

The equilibrium temperature (T_{eq}), at which $\Delta G = 0$, was calculated for each reaction. This parameter allows for precise determination of the minimum temperature required for a reaction to proceed spontaneously. The equilibrium temperature was calculated using the expression $T_{eq} = \Delta H / \Delta S$ for each reaction.

The calculated equilibrium temperatures indicate the critical onset point for the thermodynamic favorability of chloride volatilization and are essential for optimizing process conditions.

A horizontal bar chart is presented in Figure 6, showing the equilibrium temperatures (T_{eq}) for each reaction. It clearly illustrates the temperature at which each metal oxide reacts spontaneously under chlorinating conditions:

$PbO + CaCl_2 \rightarrow PbCl_2 + CaO$ —the earliest onset, with T_{eq} around 527 °C;

Cu_2O and Fe_2O_3 —mid-range equilibrium temperatures, approximately 650–730 °C;

Ni_2O_3 and Co_2O_3 —require higher chlorination temperatures, above 850 °C.

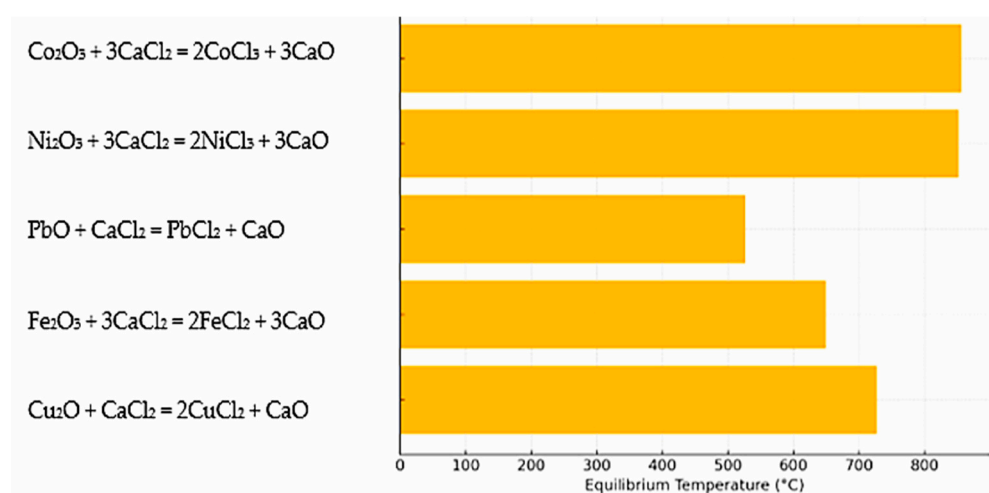


Figure 6. Energy required to reach the equilibrium temperature for chloride volatilization reactions.

Figure 7 illustrates the amount of energy (in kJ) required to heat 100 g of the charge to the equilibrium temperature (T_{eq}) for each chloride volatilization reaction:

Lead volatilization requires only approximately 40 kJ.

Copper and iron require around 50–60 kJ.

Nickel and cobalt require more than 65–70 kJ, indicating their higher energy demand for volatilization.

This analysis provides a basis for evaluating energy requirements at different stages of the chloride volatilization process, which is critical for the design of thermal regimes and heat exchange equipment.

Accordingly, both the equilibrium temperatures and the amount of energy (in kJ) required to heat 100 g of charge to these temperatures were calculated. The results indicate the following:

Lead volatilization requires only ~40 kJ;

Copper and iron require approximately 50–60 kJ;

Nickel and cobalt require more than 65–70 kJ, highlighting their greater energy demand for volatilization.

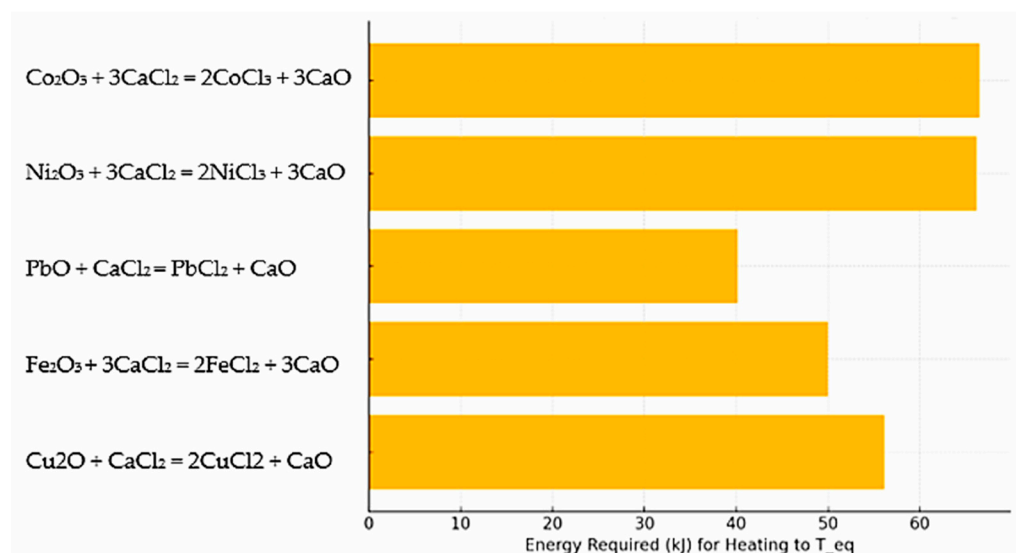


Figure 7. Calculated energy demand (in kJ) required to reach the equilibrium temperature for each chloride volatilization reaction.

The process exhibits thermodynamic staging, which enables selective volatilization of metals based on temperature:

Initial stage (600–800 °C): efficient removal of Pb, Cu, and Fe;

Elevated temperatures (900–1100 °C): required for volatilizing Ni and Co;

This enables stepwise selective chloride volatilization, beginning with Pb, followed by Fe/Cu, and finally Ni/Co.

Therefore, in a single operation, it is possible to deeply purify the concentrate from lead, zinc, and copper, while producing an iron–nickel–cobalt-containing product suitable for further processing using conventional metallurgical technologies, such as ferronickel smelting.

3. Results and Discussion

3.1. Kinetic Evaluation of the Chloride Volatilization Process

To assess the reaction rates of the chloride volatilization process, kinetic studies were carried out, including refined calculations of CaCl_2 consumption. The results include estimated reaction rate constants and activation energies for the main chloride volatilization reactions. The key reactions and their calculated activation energies are summarized in Table 5.

Figure 8 presents the dependence of the reaction rate constant (k) on the activation energy (E_a). It can be observed that, as the activation energy increases, the reaction rate constant also increases. This is attributed to the fact that the measurements were conducted at higher temperatures, which enhance the reaction kinetics despite the higher energy barrier.

Figure 9 presents the logarithmic dependence of the reaction rate constant ($\ln k$) on the activation energy (E_a) for the chloride volatilization reactions.

The linear trend confirms the exponential nature of the rate dependence, consistent with the Arrhenius equation.

Table 6 presents the linear regression equations of the form $\ln(k) = a \cdot E_a + b$ for each metal, based on the logarithmic dependence between the reaction rate constant and activation energy.

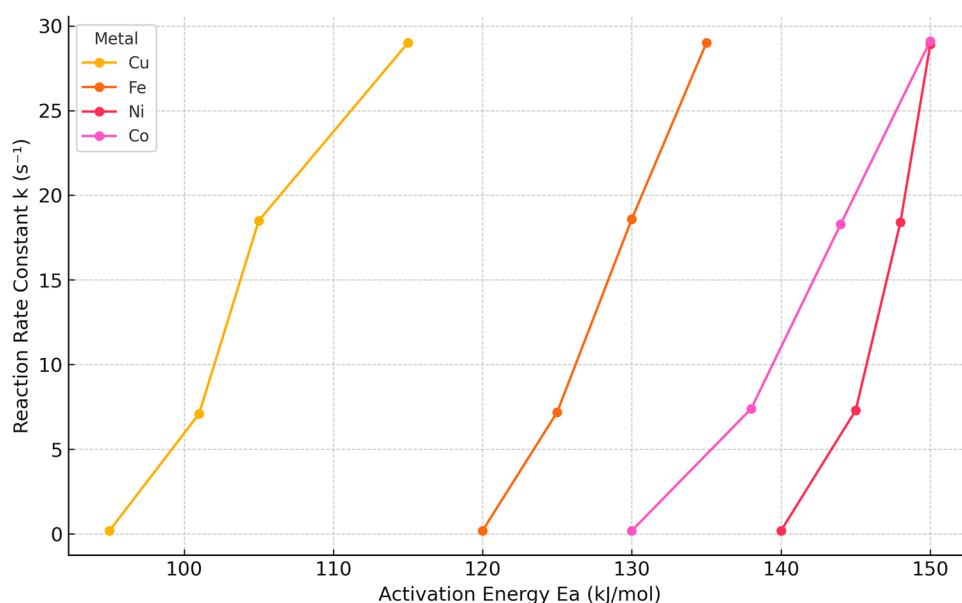
At first time represented the stepwise selective chloride volatilization process:

- Stage I (500–650 °C): removal of lead;

- Stage II (700–750 °C): chlorination of copper and iron;
- Stage III (850–900 °C): volatilization of nickel and cobalt.

Table 5. Calculated reaction rates and activation energies for the main chloride volatilization reactions.

Metal	Reaction	Theoretical CaCl ₂ Consumption (g)	Temperature (°C)	Reaction Rate Constant, k (s ^{−1})	Activation Energy, E _a (kJ/mol)
Cu	$\text{Cu}_2\text{O} + \text{CaCl}_2 \rightarrow 2\text{CuCl}_2 + \text{CaO}$	0.1226	800	0.1538	95
		0.1226	1000	7.3291	101
		0.1226	1100	18.6548	105
		0.1226	1150	28.9697	115
Fe	$\text{Fe}_2\text{O}_3 + 3\text{CaCl}_2 \rightarrow 2\text{FeCl}_2 + 3\text{CaO}$	0.244	800	0.1538	120
		0.244	1000	7.3291	125
		0.244	1100	18.6548	132
		0.244	1150	28.9697	135
Ni	$\text{Ni}_2\text{O}_3 + 3\text{CaCl}_2 \rightarrow 2\text{NiCl}_3 + 3\text{CaO}$	0.396	800	0.1538	140
		0.396	1000	7.3291	144
		0.396	1100	18.6548	148
		0.396	1150	28.9697	150
Co	$\text{Co}_2\text{O}_3 + 3\text{CaCl}_2 \rightarrow 2\text{CoCl}_3 + 3\text{CaO}$	0.608	800	0.1538	130
		0.608	1000	7.3291	138
		0.608	1100	18.6548	145
		0.608	1150	28.9697	150

**Figure 8.** Dependence of the reaction rate constant (k) on activation energy (E_a) for chloride volatilization reactions.

3.2. Technological Investigation Results of the Chloride Volatilization Process

The main objective of the experimental work was to determine the optimal technological parameters for the chloride volatilization process applied to the investigated oxide mixture.

As a result of the deep purification of the sulfide concentrate from lead, zinc, and copper by high-temperature chlorination, the following optimal process conditions were established (see Table 7). Chlorination of the charge was carried out at the specified temperature for 1.0 h. In all experiments, the weight of the oxide mixture sample was 1.0 g. The residues after chloride volatilization were analyzed for the content of Fe, Ni, Co, Cu,

Pb, and Zn. The chlorinating agent consumption, temperature, water consumption (as a percentage of the theoretically required amount), sulfur consumption (as a percentage of the charge weight), coal consumption (as a percentage of the charge weight), residue weight, and component concentrations in the residue are presented in Table 7. The extraction of charge components is shown in Table 8. The chlorinating agent consumption coefficient ranged from 1.66 to 1.7, and the charcoal consumption was 4% of the charge weight. Charcoal: Sample = $4/100 = 0.04 \Rightarrow 1.0 \text{ g (sample): } 0.04 \text{ g (charcoal)}$.

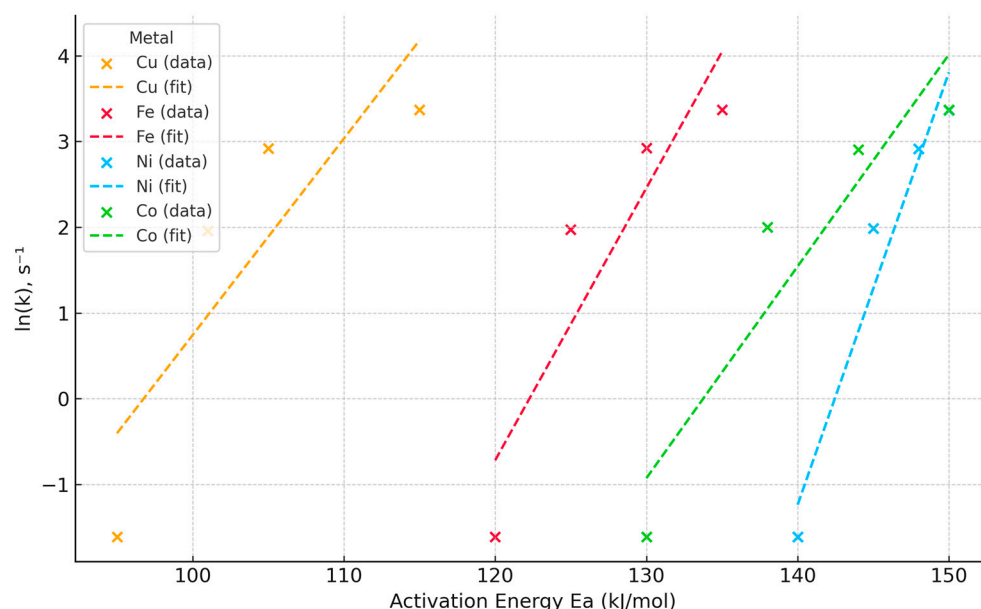


Figure 9. Logarithmic dependence of the reaction rate constant ($\ln k$) on activation energy (E_a), with linear approximation for each metal.

Table 6. Linear equations of the form $\ln(k) = a \cdot E_a + b$ for each metal.

Metal	Equation $\ln(k)$	Characteristic
Cu	$0.240 \cdot E_a - 23.33$	Moderately sensitive to temperature
Fe	$0.321 \cdot E_a - 39.46$	Rapid increase in reaction rate
Ni	$0.505 \cdot E_a - 71.82$	Highly sensitive to temperature
Co	$0.257 \cdot E_a - 34.54$	Average temperature sensitivity

Sulfur was added in varying amounts, 0%, 2%, and 3%, depending on the experiment, expressed as % of the charge weight (1.0 g), Table 7. Therefore, sulfur/sulfide addition ratio is 0.02–0.03 g per 1.0 g of sample, i.e., 1.0 g (sample):0.02–0.03 g (sulfide or sulfur).

Based on the results in Table 8, a graph was constructed showing the dependence of temperature on the extraction of charge components into the sublimates (Figure 10).

The experimental results show that Fe, Ni, and Co are minimally volatilized and remain predominantly concentrated in the roasted residue after chlorinating roasting. Pb and Zn are almost completely volatilized, while Cu is distributed between the volatilized phase and the residue. Under the applied experimental conditions, temperature had little influence on Cu volatilization. However, to enhance Cu recovery into the gas phase, it is necessary to increase the chlorinating agent dosage, reduce sulfur content in the charge, and avoid introducing water vapor and carbon into the reaction zone.

The optimal chlorination conditions were determined as follows: temperature: 1130–1150 °C; duration: 2 h; chlorinating agent ratio coefficient: 1.66–1.70; and coke consumption: 4% from the charge weight.

Under these optimized conditions, the volatilization rates of metals from the roasted sulfide concentrate (Sokolov–Sarbai Mining and Processing Association JSC) were as follows: Fe: 1.0–1.2%; Ni: 20–22%; Co: 5.0–6.5%; Pb: 98–100%; Zn: 98–100%; and Cu: 85.2–89%.

Table 7. Experimental results of chloride volatilization of the charge mixture.

Experimental Conditions					Residue Weight (g)	Components Contention in Cinder, g					
CaCl ₂ Consumption (% of Theoretical)	Temperature (°C)	Water Vapor Consumption (% of Required)	Sulfur Consumption (% of Charge Weight)	Charcoal Consumption (% of Charge Weight)		Fe	Co	Cu	Zn	Ni	Pb
140	1000	100	0	0	2.2	0.856	0.23	0.05	0.009	0.12	0.0004
					2.28	0.0861	0.2301	0.052	0.0023	0.122	0.00077
100	1150	0	3	0	2.24	0.859	0.2349	0.0875	0.00035	0.13	0.00025
					2.3	0.0857	0.235	0.086	0.00045	0.131	0.00072
100	1000	100	3	2	2.25	0.86	0.24	0.92	0.000670	0.125	0.0004
					2.01	0.0861	0.2390	0.0843	0.00104	0.1255	0.00016
140	1000	0	3	2	2.6	0.86	0.24	0.072	0.0006	0.13	0.00025
					2.47	0.0862	0.24	0.074	0.00084	0.129	0.00052
100	1150	100	0	2	2.07	0.864	0.24	0.0775	0.00285	0.125	0.00075
					2.14	0.08615	0.239	0.0778	0.0018	0.126	0.00125
140	1150	0	0	2	2.17	0.865	0.23	0.05	0.002	0.12	0.0012
					2.06	0.08620	0.2301	0.0515	0.0014	0.124	0.00098
140	1150	0	3	0	2.36	0.864	0.2349	0.055	0.00055	0.129	0.0004
					2.53	0.0863	0.2341	0.05880	0.00064	0.127	0.00113
100	1000	0	3	0	2.06	0.86	0.2298	0.0575	0.00207	0.125	0.00275
					2.21	0.086	0.2305	0.0594	0.00114	0.126	0.00098

Table 8. Extraction of charge components into sublimates, %.

Residue Weight (g)	Extraction of Charge Components into Sublimates, %					
	Fe	Co	Cu	Zn	Ni	Pb
2.2	1.5	4.2	57.7	95	20	99.75
2.28	0.9	4.08	56.1	96.14	18.4	99.53
2.27	1.2	4.14	56.9	95.57	19.25	99.64
2.24	1.2	2.1	25.8	99.42	13.4	99.84
2.3	1.4	2.04	25.3	99.25	12.3	99.56
2.4	1.3	2.07	25.55	95.33	12.85	99.7
2.25	1	0	22	98.87	16.7	99.73
2.01	0.9	0.2	28	98.3	16.36	99.9
2.1	0.95	0.1	25	98.58	16.53	99.8
2.6	1	0	39	99	13.4	99.84
2.47	1.1	0	37.2	98.6	13.7	99.68
2.5	1.05	0	38.1	98.8	13.55	99.76
2.07	0.5	0	34.3	95.25	16.7	99.53
2.14	0.87	0.2	34	97	15.8	99.23
2.2	0.685	0.1	34.15	96.12	16.25	99.38
2.17	0.4	4.2	57.7	96.67	20	99.23
2.06	0.68	4.08	56.3	97.66	18.6	99.4
2.1	0.54	4.14	57	97.16	19.3	99.31
2.36	0.5	2.1	53.3	99.08	13.7	99.75
2.53	0.64	2.6	50.1	98.93	15.2	99.31
2.6	0.57	2.35	51.7	99	14.45	99.53
2.06	0.9	4.16	51.3	96.55	16.7	99.26
2.21	1	4.01	49.6	98.1	15.8	99.4
2.3	0.95	4.085	50.45	97.32	16.25	99.83

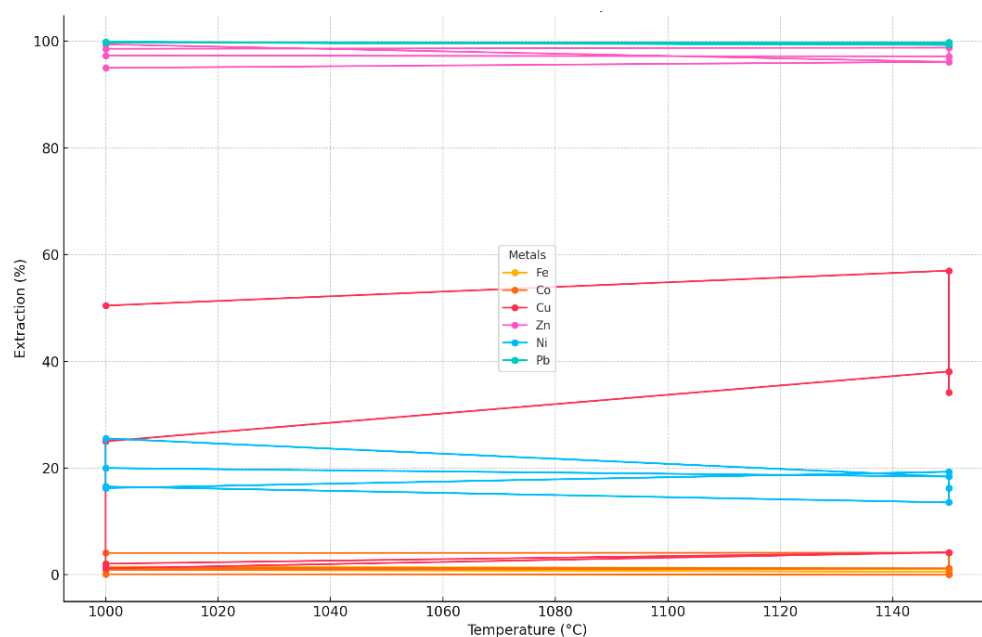


Figure 10. Extraction results of charge components into volatilized products.

These results confirm the effectiveness of high-temperature chlorination for the deep purification of sulfide concentrates from Pb, Zn, and Cu. The resulting iron–nickel–cobalt-containing product, free of Pb and Zn, is suitable for further processing using conventional technologies.

Thus, the first stage of sulfide concentrate purification from impurities has been successfully completed via selective chloride volatilization. The next stage involves the crystallization of ferric chloride solutions.

3.3. Results of the Crystallization Process of Ferric Chloride Solutions

As a result of removing non-ferrous metals from ferric chloride solutions by precipitating them in the form of sulfides, a pregnant solution remains, containing up to 180 g/L of ferrous iron and 10–30 mg/L of Co and Ni.

Further processing of ferric chloride is aimed at producing high-purity iron-containing products such as iron oxides and reduced iron. In the framework of this research, the specific focus is on obtaining iron-oxide-based pigments. Therefore, an important objective is to purify ferric chloride solutions more deeply via controlled crystallization and removal of residual non-ferrous impurities.

In the experiments, ferric chloride solutions with 162–195 g/L of Fe and 0.06–0.10 g/L of Co were used. The initial volume of solution in each experiment was 400 mL. Partial evaporation was conducted in beakers on sand baths to minimize splashing and allow for controlled concentration of the solution.

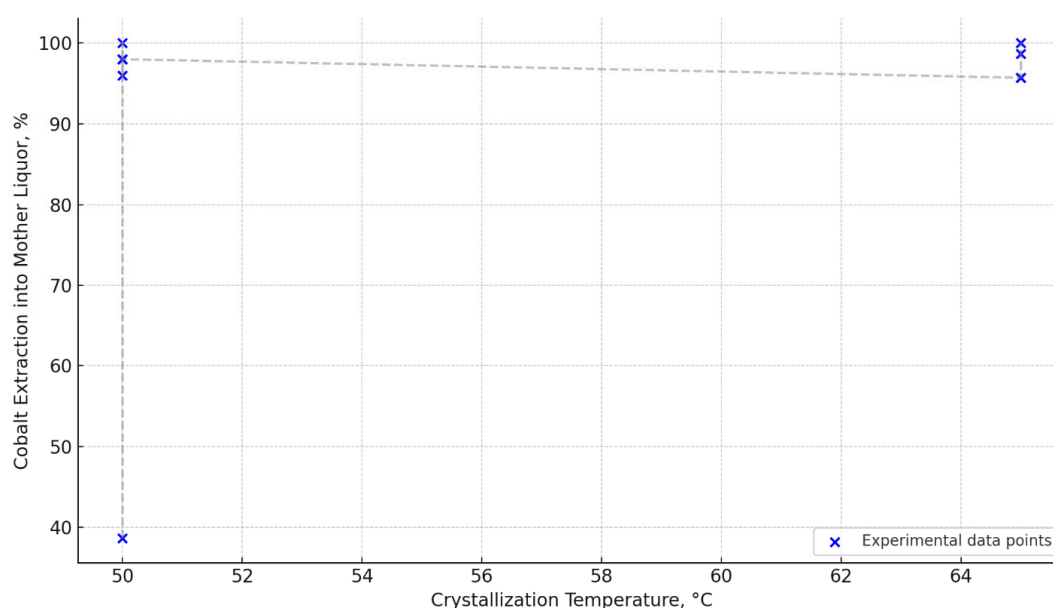
After evaporation, the solutions were cooled and crystallized in a water bath at set temperatures. The crystallization time was 1 h, performed at 50 °C and 60 °C. Upon completion, samples of the pregnant liquor were immediately collected for analysis at the crystallization temperature.

The results of the ferric chloride solution crystallization experiments are summarized in Table 9.

Table 9. Results of ferric chloride solution crystallization experiments.

Initial Co conc. (g/L)	Initial Co Amount (g)	Initial Fe conc. (g/L)	Crystallization Temp. (°C)	Volume After Evaporation (mL)	Evaporation Degree (%)	Co Conc. in Filtrate (g/L)	Co Amount in Filtrate (g)	Co Recovery (%)
0.1	40.0	162.0	50.0	350.0	12.5	0.114	39.5	98.7
0.1	40.0	162.0	50.0	300.0	25.0	0.133	40.0	100.0
0.1	40.0	162.0	50.0	350.0	12.5	0.112	39.2	98.0
0.1	40.0	162.0	50.0	300.0	25.0	0.128	38.4	96.0
0.1	40.0	162.0	50.0	350.0	12.5	0.112	39.2	98.0
0.6	24.0	189.0	65.0	200.0	50.0	0.115	23.0	95.7
0.8	32.0	195.0	65.0	350.0	12.5	0.09	31.5	98.7
0.8	32.0	195.0	65.0	300.0	25.0	0.105	31.5	95.7
0.8	32.0	195.0	65.0	250.0	37.5	0.128	32.0	100.0

Figure 11 illustrates the relationship between cobalt recovery into the pregnant liquor and the crystallization temperature.

**Figure 11.** Dependence of cobalt recovery into the pregnant liquor on crystallization temperature.

The crystallization was conducted under strongly acidic conditions ($\text{pH} < 2$), where cobalt remains soluble. No stirring was applied during the crystallization step to avoid secondary nucleation and ensure phase purity. These conditions were sufficient to ensure selective crystallization of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ without co-precipitation of cobalt or nickel.

The experimental results demonstrate that, when ferric chloride solutions are evaporated to 50% of their original volume, it is possible to obtain $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ crystals free from cobalt—as virtually all cobalt remains in the pregnant liquor.

No significant effect of temperature on cobalt partitioning was observed; complete cobalt recovery into the pregnant solution occurred at both 50 °C and 65 °C.

To explore the potential for increasing the final cobalt concentration in the pregnant liquor, a series of experiments were conducted using solutions with elevated Co content. These solutions contained 192.4 g/L of iron and 0.21 g/L of cobalt, and crystallization was performed at 65 °C.

The next stage of the study focused on the crystallization of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at room temperature. A solution containing 192.4 g/L of Fe and 0.21 g/L of Co was evaporated to 50% of its original volume. Analysis of the pregnant liquor showed that 90% of the cobalt remained in solution.

Based on the experiments, it was concluded that pure $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ crystals can be obtained from solutions containing 162–195 g/L of ferrous iron and up to 0.42 g/L of cobalt, provided that crystallization is carried out at 20 °C and the solution is evaporated by 50%.

This crystallization process was successfully performed using real ferric chloride solution obtained from hydrochloric acid processing of pyrite concentrates from JSC SSGPO (see Table 10).

Table 10. Crystallization of ferrous chloride from solutions with elevated cobalt content.

No.	Volume After Evaporation (mL)	Co Concentration in Pregnant Liquor (g/L)	Co Amount in Pregnant Liquor (g)	Co Recovery (%)	Evaporation Degree (% of Initial Volume)
1	350	0.2	70	83.3	12.5
2	300	0.253	76	90.3	25
3	250	0.31	77.5	92.2	37.5
4	200	0.42	84	100	50
5	350	0.2	70	83.3	12.5
6	300	0.251	75.4	89.8	25
7	200	0.41	82	97.6	50

The obtained crystals were analyzed using chemical and spectral methods. The impurity concentrations were determined as follows: $\text{Mg} \geq 0.001\%$; Mn —hundredths of a percent; $\text{Co} \geq 0.01\%$; $\text{Ni} \geq 0.01\%$; $\text{Cr} > 0.001\%$; $\text{Cu} < 0.01\%$; $\text{Mo} \leq 0.01\%$; and $\text{V} < 0.01\%$.

The results of the crystallization experiments confirm that deep purification of ferric chloride solutions obtained from hydrochloric acid processing of pyrite concentrates is achievable. By evaporating the solution by 50% of its original volume and performing crystallization at 20–65 °C, it is possible to obtain $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ crystals that are virtually free of cobalt and nickel.

These high-purity ferrous chloride crystals can be further processed to produce high-quality iron-based materials.

3.4. Results of High-Temperature Hydrolysis of Iron Chlorides and Production of Iron Oxide Powders

The methodology for hydrothermal decomposition of ferric chloride was described in Section 3. The obtained $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ crystals were subsequently subjected to high-temperature hydrolysis to produce iron oxide powders.

The effect of temperature and duration on the decomposition of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was investigated, and the results are presented in Table 11.

Table 11. Degree of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ decomposition depending on temperature and process duration.

Duration, min	5	10	15	20	30	40	50	60	80	100	120	180
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, T = 330 °C												
Degree of decomposition α , %	4.87	11.80	14.45	16.96	20.50	24.70	30.30	32.74	37.16	39.59	40.41	44.46
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, T = 430 °C												
Degree of decomposition α , %	19.10	25.14	29.49	31.70	35.76	43.65	50.58	58.47	70.86	86.56	93.49	95.11
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, T = 530 °C												
Degree of decomposition α , %	41.95	68.87	85.16	94.82	96.00	≈100	≈100	≈100	≈100	≈100	≈100	≈100
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, T = 630 °C												
Degree of decomposition α , %	60.53	92.83	97.40	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100	≈100

Based on the decomposition behavior of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, the following conclusions can be drawn:

At 330 °C, the decomposition progresses slowly;
 At 430 °C and above, the reaction significantly accelerates, especially in the 530–630 °C range, where near-complete decomposition is achieved in less than one hour (Figure 12).

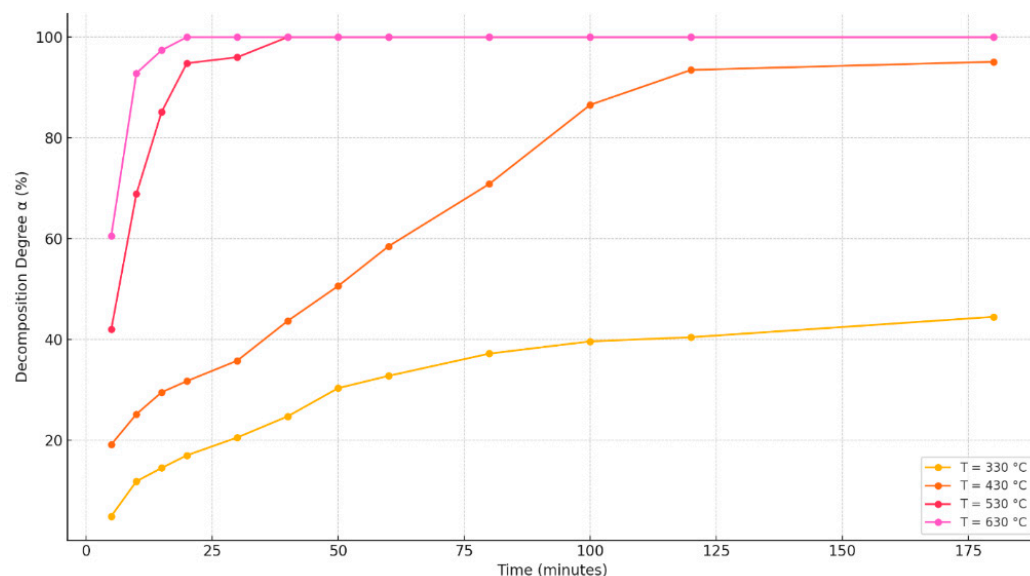
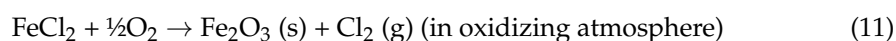
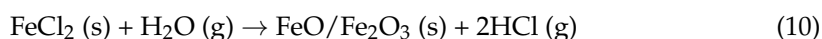
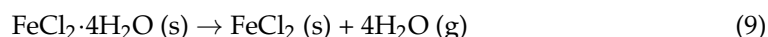


Figure 12. Dependence of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ decomposition on time and temperature.

The main possible reactions during high-temperature hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ include:



The results suggest a reaction mechanism for high-temperature hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ under oxidizing conditions.

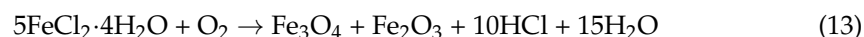
As decomposition progresses, the magnetite (Fe_3O_4) content decreases while the hematite (Fe_2O_3) content increases.

This shift is attributed to a reduction in HCl release rate, which allows more oxygen from the gas phase to diffuse into the reaction zone, favoring hematite formation alongside magnetite.

At partial decomposition ($\leq 60\%$), the main product is magnetite, corresponding to reaction (12):



At more complete decomposition, a mixture of magnetite and hematite is formed, as shown in reaction (13):



According to Figure 12, at 530 °C, the degree of decomposition $\alpha \approx 100\%$ is reached after 30–40 min, indicating nearly complete conversion of FeCl_2 .

At 800 °C (1073 K), the decomposition is even more efficient.

Even a short heating duration (15–20 min) results in near-complete breakdown of FeCl_2 .

The remaining solid product predominantly consists of Fe_2O_3 or Fe_3O_4 , depending on the atmospheric conditions.

Table 12 presents the results of the influence of the degree of development α on the composition of the solid residue.

Table 12. Effect of the decomposition degree (α) on the composition of the solid residue.

Decomposition Degree α	Residual Composition	Comment
$\alpha < 30\%$	$\text{FeCl}_2 \cdot x\text{H}_2\text{O} + \text{FeCl}_2$ partially decomposed	Chloride form dominates
$\alpha \approx 50\text{--}70\%$	$\text{FeCl}_2 + \text{FeO}/\text{Fe}_2\text{O}_3$ (mixture)	Intermediate composition
$\alpha > 90\%$	$\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$ (depending on conditions)	Oxide phases, almost no Cl^-
$\alpha \approx 100\%$	Almost pure $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$	Complete transformation

Figure 13 illustrates the phase transformation of the solid products depending on the degree of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ decomposition (α).

The decomposition mechanism of $4\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was established as follows:

- At low decomposition levels ($\alpha = 0\text{--}40\%$), the solid residue is dominated by undecomposed FeCl_2 or its hydrates;
- In the intermediate range ($\alpha = 40\text{--}80\%$), transitional phases such as FeO or Fe_3O_4 begin to form;
- At high decomposition levels ($\alpha > 90\%$), the residue consists almost entirely of Fe_2O_3 .

This behavior confirms that the decomposition degree (α) can be used as a process indicator for the completion of chloride-to-oxide conversion, which is critical for process control in chloride volatilization and for eliminating residual chloride content in the final product.

A complete mass balance of phases and volatile components during the decomposition of 10 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was calculated, and the results are presented in Table 13:

At $\alpha = 0\%$, the solid residue consists entirely of FeCl_2 (~6.38 g);

At $\alpha = 100\%$, the product is fully converted into Fe_2O_3 (~8.03 g);

As α increases, the total mass of the solid residue also increases, due to the fact that Fe_2O_3 has a higher molar mass than FeCl_2 on a per-Fe basis.

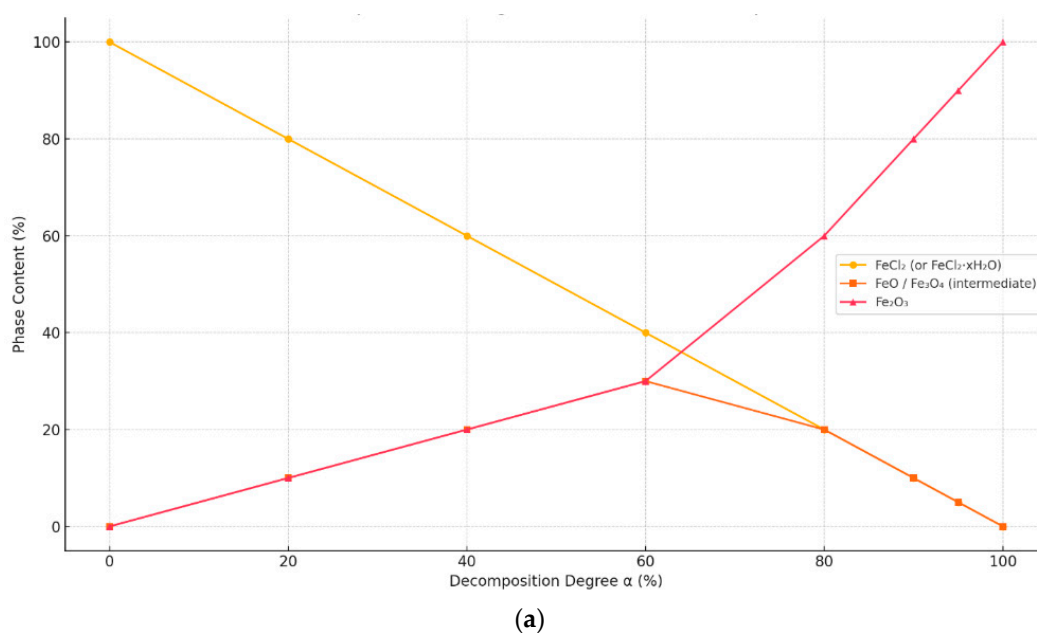


Figure 13. Cont.

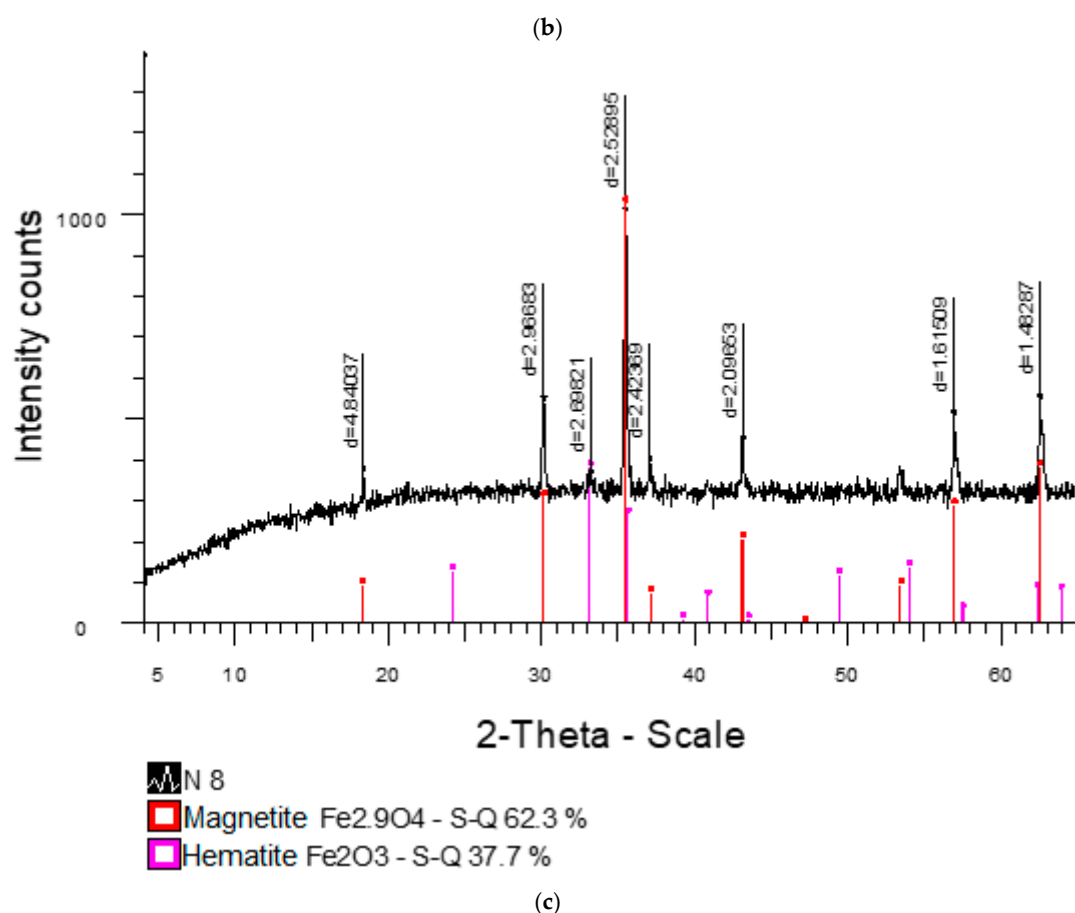
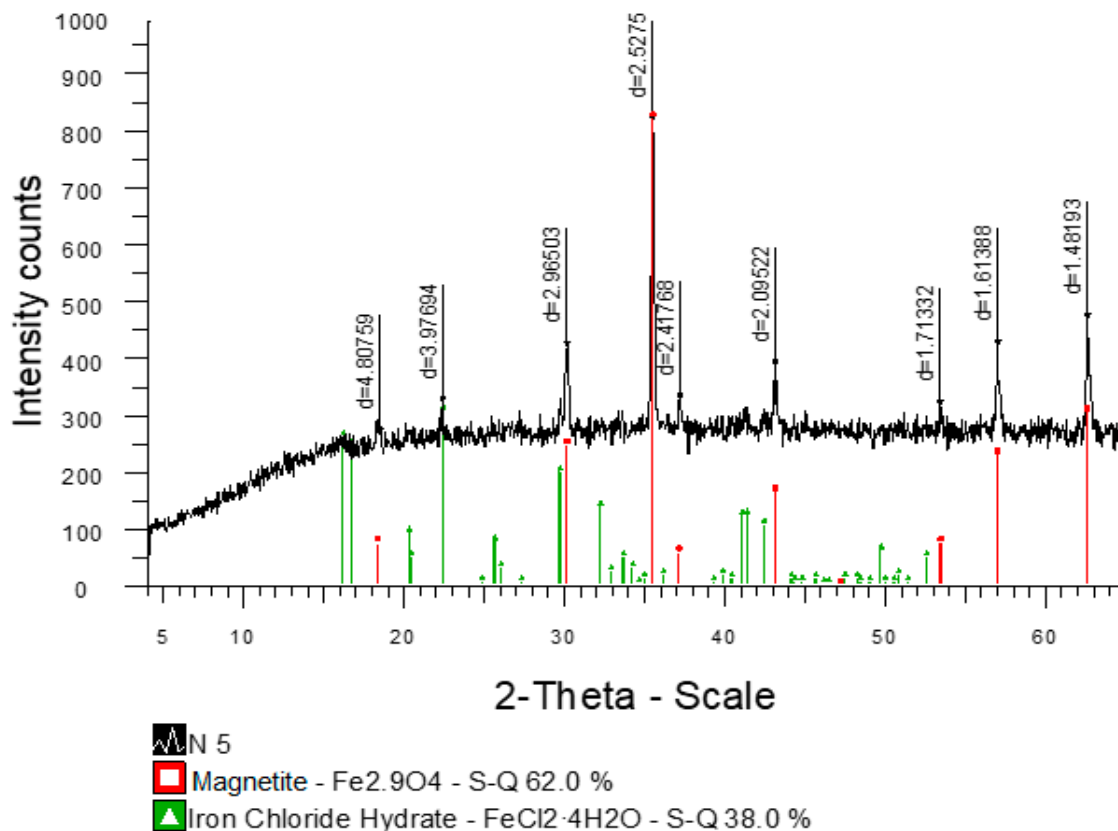


Figure 13. (a) Phase composition diagram of solid residue as a function of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ decomposition degree (α). (b) Diffraction pattern of the powder obtained by high-temperature hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at $T = 430^\circ\text{C}$. (c) Diffraction pattern of the powder obtained by high-temperature hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at $T = 630^\circ\text{C}$. Reprinted with permission from ref. [45]. 2019 Y. G. Karimov.

Table 13. Complete mass balance of phases and volatile components during the decomposition of 10 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. (1) Interplanar spacings and phase composition of the powder obtained by high-temperature hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at $T = 430^\circ\text{C}$. (2) Interplanar spacings and phase composition of the powder obtained by high-temperature hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at $T = 630^\circ\text{C}$. Reprinted with permission from ref. [45]. 2019 Y. G. Karimov.

α (%)	FeCl_2 (g)	Fe_2O_3 (g)	H_2O (g)	HCl (g)	Total Solid (g)	Total Volatile (g)	Total Mass (g)
0.0000	6.3754	0.0000	3.6246	0.0000	6.3754	3.6246	10.0000
20.0000	5.1003	1.6065	3.6246	0.7336	6.7068	4.3581	11.0649
40.0000	3.8253	3.2129	3.6246	1.4671	7.0382	5.0917	12.1299
60.0000	2.5502	4.8194	3.6246	2.2007	7.3695	5.8253	13.1948
80.0000	1.2751	6.4258	3.6246	2.9343	7.7009	6.5588	14.2597
90.0000	0.6375	7.2291	3.6246	3.3010	7.8666	6.9256	14.7922
95.0000	0.3188	7.6307	3.6246	3.4844	7.9494	7.1090	15.0584
100.0000	0.0000	8.0323	3.6246	3.6678	8.0323	7.2924	15.3247

(1)					
d , Å	I %	Mineral	d , Å	I %	Mineral
5.49178	75.0	-	2.77582	68.2	-
4.36989	59.5	-	2.52700	62.3	Magnetite
3.97457	100.0	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	2.19463	74.4	-
3.47475	59.7	-	2.18234	76.3	-
3.34786	60.3	-	2.12789	66.7	-
3.00418	89.6	-	1.73713	62.6	-

(2)					
d , Å	I %	Mineral	d , Å	I %	Mineral
4.84037	36.6	-	2.42369	39.1	-
2.96683	53.9	-	2.09653	43.9	-
2.69821	35.7	Hematite	1.61509	50.2	-
2.52895	100.0	Magnetite	1.48287	54.4	-

The X-ray phase diffractometer XPert MPD PRO (PANalytical) was used in this study. The X-ray diffraction patterns of the samples, recorded at room temperature, are shown in Figure 13b,c. The interplanar spacings and phase compositions of the samples are presented in Table 13(1,2).

Based on the data in Table 13, the particle size distribution of the obtained Fe_2O_3 powders and their specific surface area were determined (see Table 14).

Table 14. Granulometric composition and BET surface area of Fe_2O_3 powders.

α (%)	Fe_2O_3 (g)	D10 (μm)	D50 (μm)	D90 (μm)	SSA (m^2/g)
0.0000	0.0000	1.5000	2.5000	4.0000	4580.1527
20.0000	1.6065	1.2120	2.0200	3.2320	5668.5058
40.0000	3.2129	0.9240	1.5400	2.4640	7435.3128
60.0000	4.8194	0.6360	1.0600	1.6960	10,802.2469
80.0000	6.4258	0.3480	0.5800	0.9280	19,742.0374
90.0000	7.2291	0.2040	0.3400	0.5440	33,677.5932
95.0000	7.6307	0.1320	0.2200	0.3520	52,047.1895
100.0000	8.0323	0.0600	0.1000	0.1600	11,450.8168

Thus, the following data on the particle size distribution of the powders were obtained (see Table 15).

Table 15. Particle size distribution analysis.

Indicator	Tendency with Increasing α	Interpretation
D10 (μm)	decreases from 1.5 to 0.06	reducing the size of the smallest 10% particles—finer powder
D50 (μm)	decreases from 2.5 to 0.1	the median particle size is significantly reduced—the powder becomes ultrafine
D90 (μm)	decreases from 4.0 to 0.16	the size of even the largest 10% of particles decreases—the range of sizes narrows
Δ (D90–D10)	narrows from 2.5 to 0.1	indicates a narrower particle size distribution at high α

The SSA values (m^2/g) increase sharply from $4580.1 \text{ m}^2/\text{g}$ at $\alpha = 0\%$ to $11450.8 \text{ m}^2/\text{g}$ at $\alpha = 100\%$. This is an exponential growth associated with a decrease in particle size and an increase in their specific surface area. The SSA value is inversely proportional to the particle diameter. The transition from the micron to the submicron and nanometer scale leads to a drastic increase in surface area. Controlling the α parameter allows regulation of powder dispersion and activity; at low α values (up to 40%), powders with $D50 > 1.5 \mu\text{m}$ and low SSA are obtained—suitable for ceramics, coatings, and fillers; at high α values ($>90\%$), nanopowders with $\text{SSA} > 30,000 \text{ m}^2/\text{g}$ are formed—these are highly active materials for catalysts, pigments, and sorbents.

The conducted experiments lead to the following conclusions: to obtain ultrafine Fe_2O_3 with high SSA, it is advisable to carry out thermal decomposition up to $\alpha = 95\text{--}100\%$. If a controlled fraction or target D50 is required, α should be limited to the range of 40–60%. Process temperature/time optimization should aim to minimize agglomeration at high α levels.

A diagram (Figure 14) was developed to illustrate how the masses of individual solid phases (FeCl_2 and Fe_2O_3), as well as the total mass of the solid residue, change with increasing decomposition degree (α):

The mass of FeCl_2 decreases linearly with increasing α ;

The mass of Fe_2O_3 increases linearly as α increases;

The total mass of the solid residue increases with α , which is important to consider in solid product yield calculations and equipment loading estimates.

A stacked diagram was constructed to show the phase distribution of mass components during the thermal decomposition of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

With increasing decomposition degree (α):

The mass of FeCl_2 decreases;

The masses of Fe_2O_3 and HCl increase;

The mass of H_2O remains constant, as it is entirely released during dehydration, regardless of α .

Figure 15 provides a clear visual representation of the evolution of solid and volatile phases during decomposition and serves as a valuable tool for conducting mass and energy balance calculations in process engineering.

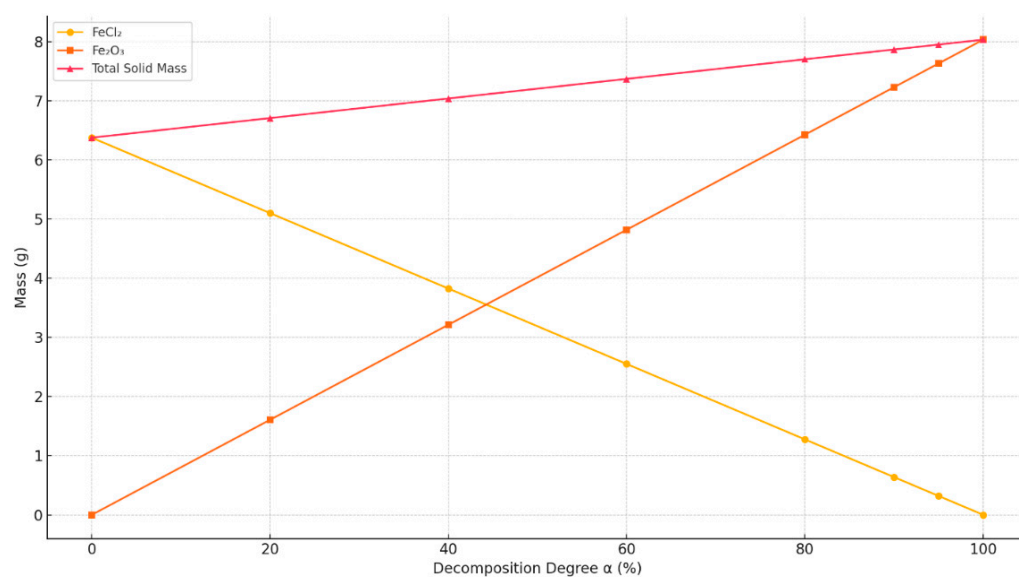


Figure 14. Mass decomposition diagram of FeCl₂ and Fe₂O₃ as a function of FeCl₂·4H₂O decomposition degree (α).

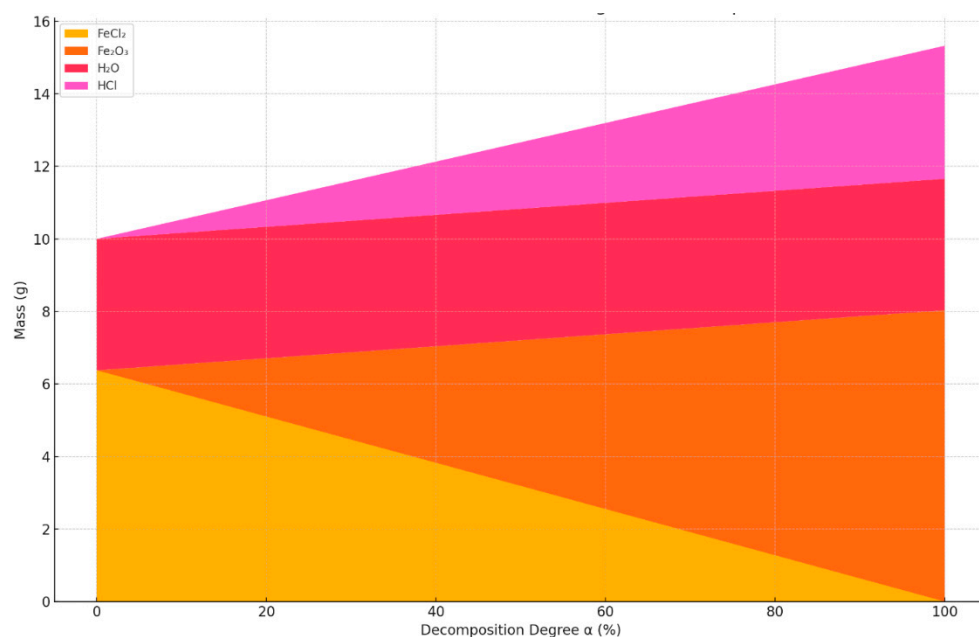


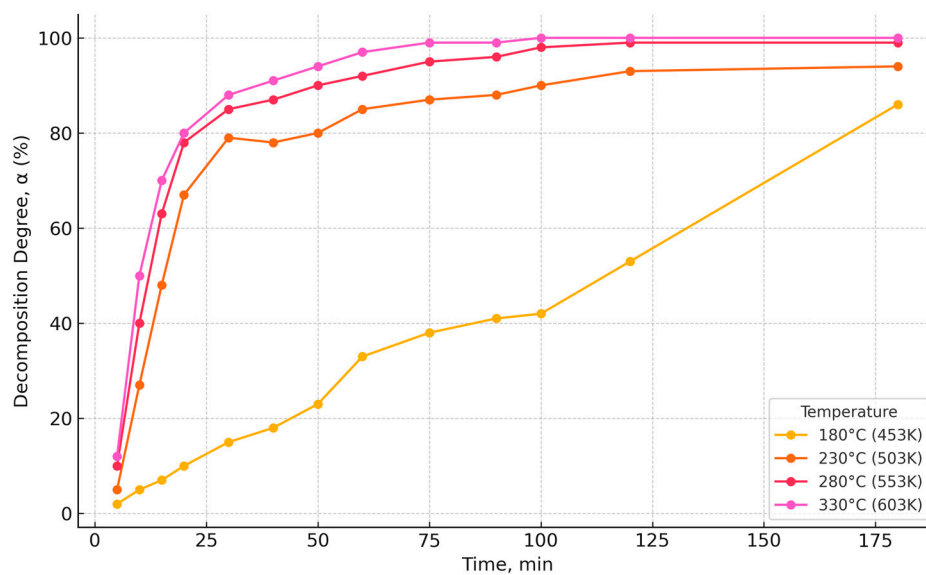
Figure 15. Stacked diagram of phase mass distribution during the decomposition of FeCl₂·4H₂O.

3.5. Investigation of the Mechanism and Kinetics of High-Temperature Hydrolysis of FeCl₃·6H₂O Crystals in an Oxidizing Atmosphere

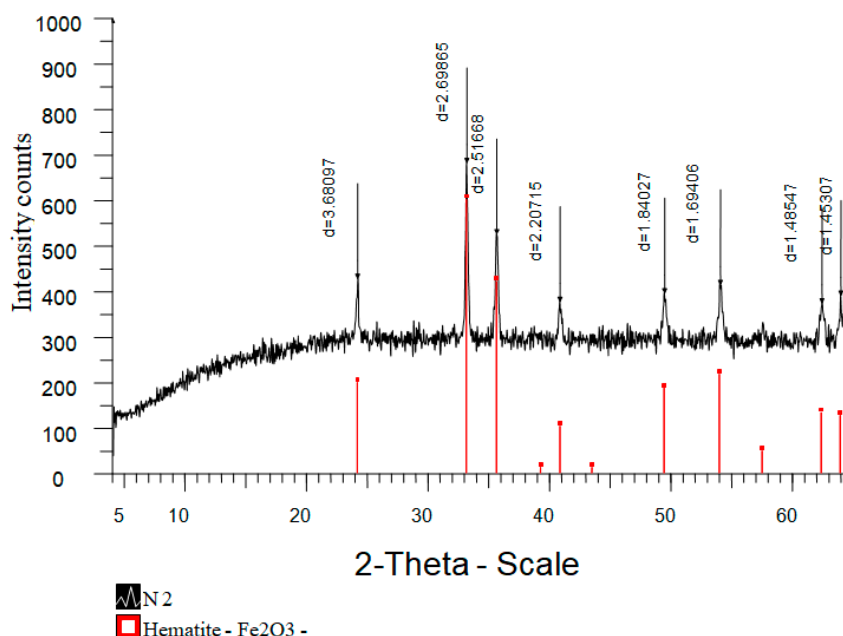
The methodology for high-temperature hydrolysis is described in Section 3.5. The results of FeCl₃·6H₂O crystal decomposition at various temperatures and durations are summarized in Table 14.

Figure 16 illustrates the dependence of the decomposition degree of ferric chloride (FeCl₃·6H₂O) on temperature and reaction time.

The obtained results indicate that nearly complete decomposition of FeCl₃·6H₂O occurs at temperatures above 553–603 K within 60 min. When the hydrolysis temperature is reduced to 503 K or lower, the decomposition rate decreases significantly and, even after 180 min, complete decomposition is not achieved (see Table 16 and Figure 16).



(a)



(b)

Figure 16. (a) Dependence of the decomposition degree of ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) on temperature and duration. (b) Diffractogram of powder obtained by high-temperature hydrolysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ $T = 330^\circ\text{C}$. Reprinted with permission from ref. [45]. 2019 Y. G. Karimov.

Table 16 shows the interplanar distances and phase composition of the powder obtained by high-temperature hydrolysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ $T = 330^\circ\text{C}$. Figure 16 shows the diffraction pattern of the powder obtained by high-temperature hydrolysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ $T = 330^\circ\text{C}$. Table 16(2) shows the results of semi-quantitative X-ray phase analysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ hydrolysis powders.

Table 16. Decomposition degree of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ depending on temperature and process duration. (1) Interplanar distances and phase composition of the powder obtained by high-temperature hydrolysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ $T = 330^\circ\text{C}$. (2) Results of semi-quantitative X-ray phase analysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ hydrolysis powders. Reprinted with permission from ref. [45]. 2019 Y. G. Karimov.

Duration, min	5	10	15	20	30	40	50	60	80	100	120	180
FeCl ₃ ·6H ₂ O, T = 180 °C												
Degree of decomposition, α %	0.00	5.13	6.59	7.83	12.39	18.19	23.10	32.95	37.91	41.40	52.50	86.30
FeCl ₃ ·6H ₂ O, T = 230 °C												
Degree of decomposition, α %	0.00	25.44	47.04	68.14	77.57	78.41	81.23	85.23	88.55	91.65	94.01	94.92
FeCl ₃ ·6H ₂ O, T = 280 °C												
Degree of decomposition, α %	3.83	43.88	63.09	77.45	83.93	88.72	96.32	≈100	≈100	≈100	≈100	≈100
FeCl ₃ ·6H ₂ O, T = 330 °C												
Degree of decomposition, α %	10.48	48.11	67.37	79.65	85.68	89.68	97.00	≈100	≈100	≈100	≈100	≈100
(1)												
<i>d</i> , Å			<i>I</i> %		Mineral			<i>d</i> , Å		<i>I</i> %		Mineral
2.70594			100.0		Hematite			2.10782		73.2		-
2.55417			86.4		-			1.48704		82.1		-
2.51626			89.3		-			-		-		-
(2)												
Products Composition				Formula				Contention, %		Hydrolysis Temperature, °C		
Hematite				Fe ₂ O ₃				100		330		

Experiments conducted to study the effect of the decomposition degree of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ crystals on the composition of oxide products formed during high-temperature hydrolysis revealed that the decomposition degree does not influence the phase composition, since gaseous oxygen does not participate in the reaction. The resulting powders consist of hematite, formed according to the following reaction:

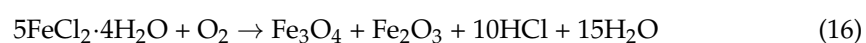


In contrast, the hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ yields different results depending on the decomposition degree.

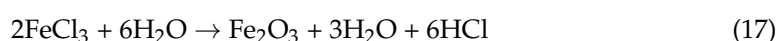
At partial decomposition ($\leq 60\%$), the main product is magnetite, formed via:



At higher decomposition degrees, a mixture of magnetite and hematite is formed:



For $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, however, the final product is hematite, regardless of temperature and duration, and the hydrolysis proceeds consistently via:



The high-temperature hydrolysis of both $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in a stationary bed under oxidizing conditions exhibits a topokinetic behavior, indicating that nucleation and growth of the new oxide phase occur on the surface of the iron chloride crystals.

Thus, iron oxide powders of defined composition were successfully synthesized by high-temperature hydrolysis. The results are summarized in Table 17.

Table 17. Composition of iron oxide powders.

Phase	Formula	Mass Fraction (%)	Notes
Magnetite	Fe_3O_4	60–80	Main product at ~60% decomposition
Hematite	Fe_2O_3	10–30	Appears at higher decomposition degrees (>60%)
Residual iron chloride	FeCl_2	0–10	Remains if decomposition is incomplete

3.6. Investigation of the Composition and Properties of Powders Obtained by High-Temperature Hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ Using Physicochemical Methods

A set of experiments was conducted to study the composition, structure, and properties of the powders produced through high-temperature hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

The results (Table 17) indicate that, at a hydrolysis temperature of 430 °C, the powder contains 38% iron(II) chloride, 62% magnetite, and no hematite was detected.

At a temperature of 630 °C, no iron chloride was found in the solid product. The phase composition consisted of 62.3% magnetite and 37.7% hematite (see Figures 16b and 17).

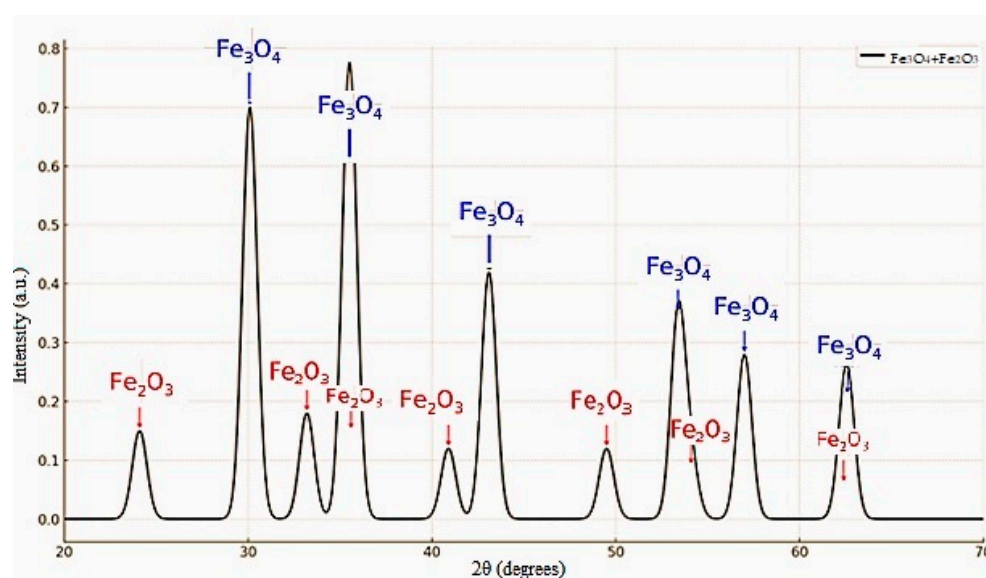


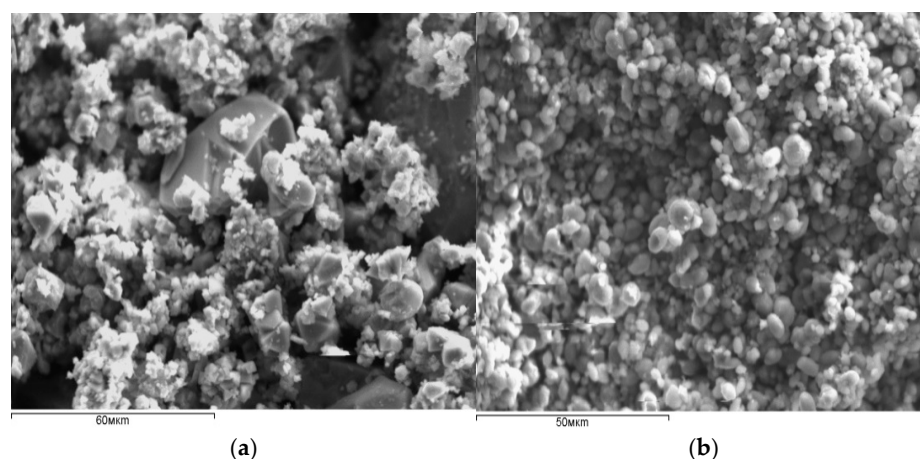
Figure 17. X-ray diffraction (XRD) pattern of the obtained powder.

To determine the dispersion of the oxidized iron powder and the elemental composition of microinclusions, an electron microprobe analysis was performed. The morphological characteristics of the powder were also examined, including particle geometry, as well as the presence of pores and cracks.

The results of the elemental composition analysis of microinclusions in the powders obtained by hydrothermal decomposition of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ are summarized in Table 18, and the corresponding micrographs of the powders are shown in Figure 18.

Table 18. EDS results of elemental composition analysis of microinclusions in powders obtained by hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

Temperature, °C	Element Content, %			
	O	Cl	Fe	Total
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$				
430	24.3	13.2	62.5	100.00
630	27.6	-	72.4	100.00
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$				
603	29.55	-	70.45	100.00

**Figure 18.** Electron microprobe images of powders obtained by high-temperature hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. (a) At 630 °C from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; (b) at 330 °C from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

The materials obtained after hydrolysis are ultrafine iron oxide powders with particle sizes smaller than 50 µm. Table 17 presents the results of X-ray phase analysis of the content of elements in powders.

The elemental composition analysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ microinclusions shows that, at a hydrolysis temperature of 430 °C, the chlorine content was 13.2%, while, at 630 °C, no chlorine was detected. The percentage of iron and oxygen at 430 °C corresponds to the stoichiometry of magnetite, whereas, at 630 °C, it corresponds to a mixture of magnetite and hematite.

The elemental analysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ decomposition products revealed no detectable chlorine. The iron and oxygen contents are consistent with the stoichiometric composition of hematite.

The microstructure consists of spheroidal and plate-like particles, with smooth and rough surfaces. In SEM images of the samples, microcracks are observed in particles with sizes of 50 µm and 10 µm.

Microdispersed particles (<50 nm) were detected in both $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ samples, indicating high nucleation rates and limited crystal growth during high-temperature hydrolysis. The dominance of spherical particles is attributed to minimization of surface energy during particle formation. The presence of rhombic and triangular morphologies is likely related to oriented growth of magnetite and hematite crystals along specific crystallographic directions.

High nucleation during the thermal hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Figures 18–20) is confirmed by:

→ The formation of ultrafine particles (5–30 nm);

- A sharp increase in specific surface area (SSA);
- Spherical, well-dispersed particle morphology;
- Limited crystal growth even at high decomposition degrees.

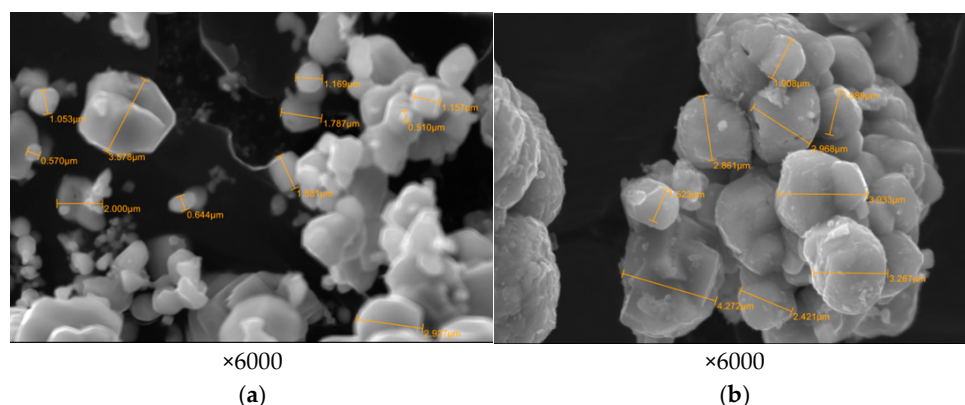


Figure 19. Scanning electron microscopy (SEM) images of iron oxide powders obtained at a hydrolysis temperature of 630 °C. (a) At 630 °C, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; (b) at 630 °C, $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$.

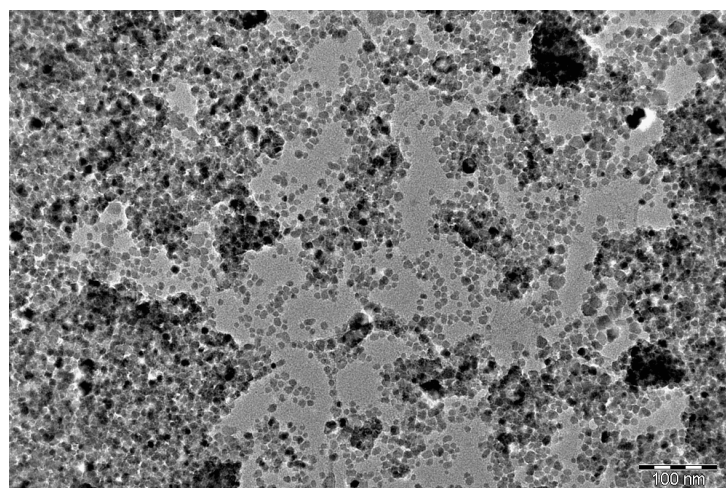


Figure 20. SEM results of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at 630 °C under $\times 30,000$.

Thus, high nucleation is an advantage when you want to obtain fine, active, homogeneous powders. This was the main goal in applying metallurgical technology for obtaining powders from non-ferrous metal concentrates.

Scanning electron microscopy (SEM) was performed using a JEOL JSM-6610LV scanning electron microscope (Japan, 2013). Figure 19 shows SEM micrographs of the product obtained by high-temperature hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at 630 °C under experimental processing conditions.

SEM micrographs of the iron oxide powders produced by high-temperature hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ show that the material predominantly consists of rounded particles. In addition, rhombic and triangular particles are also observed.

The SEM results confirm the presence of ultrafine particles with sizes below 50 μm .

In the micrographs of powders obtained from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, higher-resolution images reveal particles up to 500 μm that form larger agglomerates.

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ powders were also obtained by high-temperature hydrolysis at 630 °C with a finer dispersion than 50 μm , as well as powders with a dispersion of 100 μm ; see SEM micrographs in Figure 20.

The particle size distribution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at 630°C was defined according to SEM analysis; Figure 20 and represented on Figure 21.

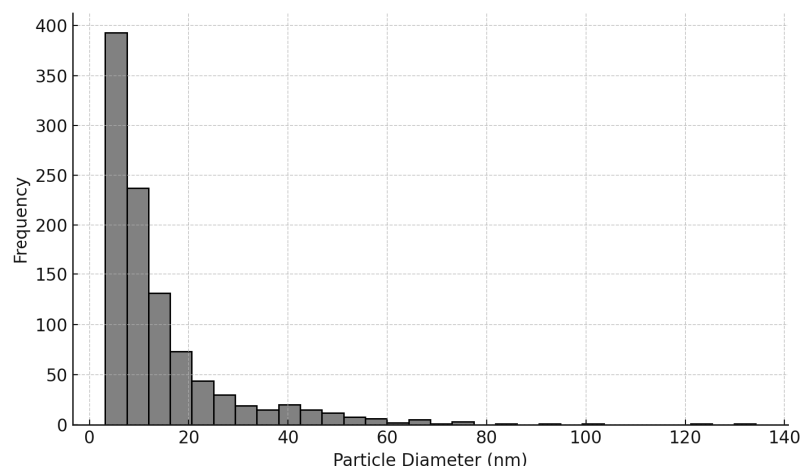


Figure 21. Particle size distribution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at 630°C .

The powders of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ can be confidently classified as nanodispersed, since the bulk of the particles are less than 100 nm in size. Also predominant particle size can be defined: 5 to 30 nm; maximum recorded size: up to 130–140 nm; single inclusions, average size (visually estimated): about 15–25 nm. Morphology: particles are mostly spherical, well-dispersed phases.

The results obtained by transmission electron microscopy confirm the scanning electron microscopy findings; the samples are represented by ultrafine iron oxide powders with particle sizes of less than 100 nm, predominantly having a spherical shape.

Specific surface area (SSA) was defined by BET analysis (BET nitrogen adsorption method) with accounting formula.

To estimate the SSA, a BET-like approximation formula can be applied, assuming spherical particles:

$$\text{SSA} = 6 / \rho \cdot d \quad (18)$$

where SSA is the specific surface area (m^2/g), ρ is the material density (g/cm^3), and d is the average particle diameter (in cm).

For Fe_2O_3 :

$$\rho = 5.24 \text{ g}/\text{cm}^3$$

Assuming an average particle size of $40 \text{ nm} = 4 \times 10^{-6} \text{ cm}$:

$$\text{SSA} \approx 6 / 5.24 \cdot 4 \cdot 10^{-6} \approx 286 \text{ m}^2/\text{g} \quad (19)$$

Estimated result: the specific surface area may reach approximately $200\text{--}300 \text{ m}^2/\text{g}$, which is typical for ultrafine metal oxide powders.

Summary of findings:

- High-temperature hydrolysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is preferable for producing high-purity hematite;
- $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ hydrolysis yields magnetite and, with further decomposition, a mixture of magnetite and hematite;
- The temperature range of $627\text{--}677^\circ\text{C}$ is optimal for producing a stable pigment mixture;
- The composition of the pigment can be finely tuned by adjusting hydrolysis time and temperature;

- Desired pigment color properties can be obtained: Fe_2O_3 —bright red; Fe_3O_4 —dark gray or black;
- The results of SSA are $286 \text{ m}^2/\text{g}$.

3.7. Production of Iron Oxide Pigments Fe_2O_3 and Fe_3O_4

Based on the literature review and the experimental data obtained from the high-temperature hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, an algorithm was developed for producing iron-containing pigments with controlled composition and color. This includes calcination (drying) conditions, color palette, and the composition of final products. The approach is particularly relevant for the synthesis of magnetite–hematite-type pigments with tunable optical properties (ranging from black to red–brown tones).

The general process flow for pigment production includes the following steps:

Initial raw material: pyrite–cobalt concentrate

→ chloride volatilization with CaCl_2 ;

Condensation of FeCl_2 vapors

→ precursor formation: $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$;

Alternative route: dissolution of Fe^{3+}

→ crystallization;

→ precursor formation: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

Based on the pigments obtained, the dominant phase and color characteristics were determined (see Table 19).

Table 19. Results of high-temperature hydrolysis in the presence of oxygen for the production of Fe_2O_3 and Fe_3O_4 pigments.

Conditions	Dominant Phase	Pigment Color
430 °C, $\alpha \approx 60\%$	Fe_3O_4 (magnetite, ~62%), residual FeCl_2	Black/dark gray
630 °C, $\alpha > 60\%$	Fe_3O_4 (62%) + Fe_2O_3 (38%)	Dark brown
727–827 °C, $\alpha \approx 100\%$	Fe_2O_3 (hematite, >90%)	Red–brown/red

To stabilize the properties, color, and composition of the obtained powders, a sequence of washing, drying, and calcination steps is performed (see Table 20):

- Removal of residual FeCl_2 : washing with 1–2% NaOH solution, followed by rinsing with distilled water;
- Drying at 110–120 °C;
- Calcination conducted in a muffle furnace at 600–1000 °C.

It was established that drying and calcination of the samples result in the formation of a color palette of pigments, depending on their composition (see Table 21).

It was found that the color change in iron-containing pigments during increased drying and calcination temperatures is associated with the following factors:

1. Phase transformations and compositional changes:

At low temperatures (400–600 °C), Fe_2O_3 (hematite) is the dominant phase—a red pigment. Hematite particles are fine, amorphous, or poorly crystallized, reflecting more light in the red spectrum.

At higher temperatures (700–900 °C), partial reduction of hematite to magnetite (Fe_3O_4) occurs, especially in low-oxygen atmospheres or under residual moisture. Magnetite is black with a metallic luster and absorbs almost the entire visible spectrum → results in dark red or brownish-black tones.

2. Crystal growth and packing density:

Increasing temperature leads to grain growth (sintering): density increases and porosity decreases;

Fine pigments scatter light more effectively → brighter colors;

Coarse pigments absorb more light → darker tones.

3. Calcination atmosphere:

Under oxidizing conditions, hematite (Fe_2O_3) remains stable → the color stays red up to 900–1000 °C;

In low-ventilation or reducing environments, partial reduction of Fe^{3+} to Fe^{2+} may occur → formation of Fe_3O_4 or FeO (magnetite) → resulting in darker pigment shades.

4. Partial conversion of hematite to magnetite:



This reaction occurs at elevated temperatures in the presence of reducing agents (e.g., steam, organics, and CO), leading to corresponding color changes (see Table 22).

Table 20. Calcination conditions and their effects.

Calcination Temperature	Duration	Atmosphere	Effect
400 °C	1 h	Air	Enhancement of red color (hematite)
600–700 °C	1–2 h	Air	Color deepening, crystal growth
800–900 °C	1–2 h	Air	Intense red color, increased Fe_2O_3 content
1000 °C	1 h	Air	Pure hematite, maximum crystallinity

Table 21. Pigment color palette depending on composition.

Pigment Composition (wt.%)	Fe_3O_4 (%)	Fe_2O_3 (%)	Color	Application
90–100% Fe_3O_4	≥90	0–10	Black	Primers, masking agents
70% Fe_3O_4 / 30% Fe_2O_3	70	30	Dark brown	Metal coatings
50% Fe_3O_4 / 50% Fe_2O_3	50	50	Brown	Construction mixtures
20% Fe_3O_4 / 80% Fe_2O_3	20	80	Red–brown	Architectural pigments
≥90% Fe_2O_3 (hematite)	0–10	≥90	Red	Ceramics, paints

Table 22. Conditions for pigment color change.

Temperature (°C)	Main Phase	Pigment Color
400–600	Fe_2O_3 (hematite)	Red
700–800	Fe_2O_3 + Fe_3O_4	Red–brown
900–1000	Fe_3O_4 dominates	Dark red/black

The general characteristics of calcined pigments are presented in Table 23.

A color palette of the pigments obtained from pyrite–cobalt concentrates via high-temperature hydrolysis has been developed (see Figure 22).

Table 23. General characteristics of calcined pigments.

Calcination Temperature	Main Phase	Color	Crystallinity	Porosity	Magnetism
400 °C	Fe ₂ O ₃	Dark red	Medium	High	Non-magnetic
700 °C	Fe ₂ O ₃	Bright red	High	Medium	Non-magnetic
900 °C	Fe ₂ O ₃	Intensely red	Very high	Low	Non-magnetic
1000 °C	Fe ₂ O ₃	Dark red	Maximum	Very low	Non-magnetic
600–800 °C (Fe ₃ O ₄ dominates)	Fe ₃ O ₄	Red-black/Brown	High	Medium	Ferromagnetic

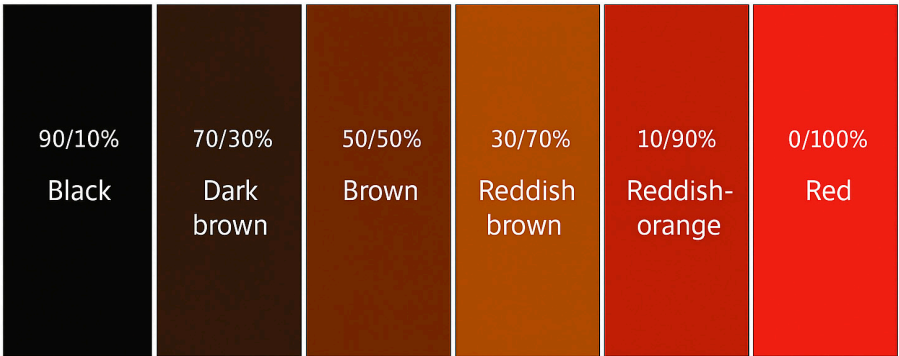


Figure 22. Visual color palette corresponding to different Fe₃O₄/Fe₂O₃ pigment ratios, from black (magnetite) to red (hematite).

Figure 23 shows a photograph of the obtained pigment with Fe₂O₃ composition.



Figure 23. Photograph of the Fe₂O₃-based pigment (hematite).

4. Conclusions

A novel technological scheme (Figure 24) has been developed for the comprehensive processing of pyrite–cobalt concentrates aimed at obtaining high-purity iron oxide pigments (Fe₃O₄ and Fe₂O₃) via a combination of oxidizing roasting, selective chloride volatilization, and high-temperature hydrolysis. The proposed method ensures the efficient removal of non-ferrous impurities and allows for the production of ultrafine iron oxide powders with controlled composition and color properties.

The resulting Fe₃O₄/Fe₂O₃ pigments represent value-added microdispersed and nanodispersed materials with broad industrial applications in construction, coatings, and ceramics. Importantly, the proposed process enables the recovery and utilization of strategic metals such as cobalt and nickel, contributing to the sustainable management of mineral resources.

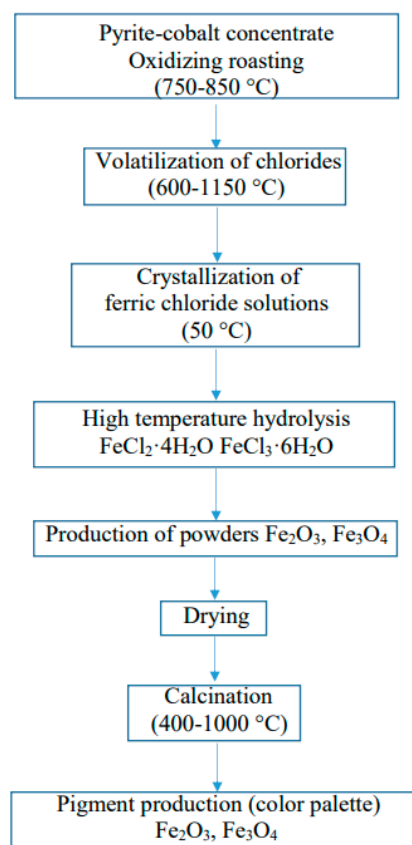
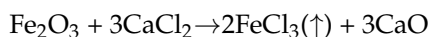
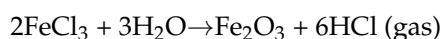


Figure 24. General technological flowchart for the processing of pyrite–cobalt concentrate.

The following economic indicators of the technology have been developed:
During chloride volatilization:



During hydrolysis:



Theoretical HCl yield: ~300–400 kg per ton of concentrate. Current recovery efficiency: ~50–60%, depending on condensation and capture systems. The economic effect consists of the following points: industrial HCl price: ~USD 200/ton; recovered HCl: ~180–200 kg → savings of USD 36–40 per ton; this is not included in revenue but reduces reagent costs in closed-loop operations. The key cost variables (CaCl₂, energy, and HCl recovery) have been quantified and can be optimized; increasing HCl capture efficiency >70% may yield savings of up to USD 50/ton; reducing energy consumption through heat integration may lower energy costs by USD 3–5/ton; using recycled or industrial-grade CaCl₂ could cut reagent costs by 30–40%; the final pigment product (Fe₃O₄/Fe₂O₃) achieves a profit margin of ~40.6%, even at moderate selling prices (USD 1.5/kg). Higher profitability is possible with red pigments (up to USD 2.5/kg).

The yield of pigments from 1 tonne of concentrate reaches 270 kg, with an estimated market value of USD 1.2–2.0 per kg, resulting in a projected revenue of approximately USD 405 per tonne and a profitability of 40.6%.

Thus, the developed technology offers both scientific novelty and commercial potential, making it attractive for scaling up and industrial implementation.

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Abbreviations

The following abbreviations are used in this manuscript:

SSGPO	Sokolov–Sarbai Mining and Processing Production Association
JSC	Joint Stock Company
CATL	Contemporary Ampere Technology Co., Limited

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