ABSTRACT

to the thesis of **IGOR MOTOVILOV**
on the theme **“PROCESSING OF IRON CHLORIDE SOLUTION”**,
presented for Doctor of Philosophy (PhD) degree by
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Assessment of the current state of a scientific or technological problem being solved. An analysis of the world market for ultrafine powders demonstrates the widespread use of powders in knowledge-based and high-tech spheres of human activity. Due to their availability, high processability of production processes and low toxicity for the human body, ultrafine powders of iron oxides are promising materials for industry and medicine.

Mainly physical and chemical methods are used to obtain ultrafine powders. As a rule, physical methods require high energy costs, which increase the cost of the final product. The use of chemical and chemical-metallurgical methods allows reducing the cost of the finished product, and, in some cases, has certain technological advantages, for example, the ability to control the size and shape of particles by chemical methods, to obtain particles with a narrow size distribution, which is necessary to obtain stable magnetic liquids and high-quality composite coatings.

A significant amount of work has been done in the world on this topic; however, many aspects of the preparation of ultrafine iron oxide powders with desired properties require further study. The task of developing new or improving already-existing methods for producing ultrafine oxide powders is currently relevant for Kazakhstan, where the potential need for ultrafine powders of iron oxides is 5-10 thousand tons per year.

The main disadvantage of the known processes is the use of expensive raw materials. Production waste and secondary raw materials have been used as a source of raw materials in this work.

Along with the main products in non-ferrous and ferrous metallurgy by-products (iron-containing materials, pickling solutions, pyrite raw materials, recycled materials) are distinguished, processing of which until the final product using existing technologies is not always economically profitable.

These products can be processed by economical hydrochloric acid technology using leaching processes, purification of solutions from impurities, crystallization, high-temperature hydrolysis to produce iron oxide powders and regeneration of hydrochloric acid.

A technological scheme has been developed in the thesis for producing powders of oxidized iron using the process of high-temperature hydrolysis from solutions of iron chloride purified from impurities.

The basis and initial data for the research into the topic. The basis for the research into the topic is the need and the possibility of organizing the production of ultrafine iron oxide powders in Kazakhstan with involvement in the production of by-products and dumped ferrous and non-ferrous metallurgy.

In the thesis the technology of high-temperature hydrolysis of ferric chloride solutions, obtained as a co-product in the hydrometallurgical processing of raw materials of Kazakhstan, is taken as a source data for the research into the topic on the basis of a critical analysis of the literature on the processing of ferric chloride solutions.

Relevance of the thesis topic. The relevance of the work is associated with the general problem of obtaining ultrafine powders and products based on them, which have a set of properties and are intended for the use in various fields of science and technology, including power engineering. The synthesis of ultrafine powders with a high specific surface is of interest from the standpoint of their catalytic activity, and ultrafine (less than 10 nm) is of concern from the point of view of their magnetic characteristics. Analysis of the literature indicates the need to solve the problem of producing these types of powders, as well as the problems of utilization of metallurgical production wastes.

Based on the above it follows that the choice of this dissertation work research direction is relevant, and the results obtained in the course of the work have scientific and practical significance.

The novelty of the topic lies in the development of a closed technology for processing solutions of ferric chloride by high-temperature hydrolysis to produce ultrafine powders of iron oxides of a given composition and regeneration of hydrochloric acid.

The scientific novelty of the results obtained:

– thermodynamically, with the decomposition of iron chloride, magnetite and hematite with the formation of hematite should be formed together. It has been established that predominantly magnetite is primarily formed during decomposition, and with an increase in the degree of decomposition of iron chloride, the hematite content in high-temperature hydrolysis of $FeCl_2$*$4H_2O$ crystals increases, which is caused by a change (decrease) in the release rate of the gaseous reaction product - HCl with increasing degree of chloride decomposition. This leads to an increase in the rate of oxygen diffusion of the gas phase into the reaction zone, which entails the formation of hematite together with magnetite.

The final products of high-temperature hydrolysis of $FeCl_2$*$4H_2O$ crystals with incomplete decomposition (not more than 60%) are magnetite, and with more complete decomposition it is a mixture of magnetite and hematite powders;

– process of high-temperature hydrolysis of $FeCl_2$*$4H_2O$ and $FeCl_3$*$6H_2O$ in a stationary layer in the presence of oxygen has a topokinetic character, which indicates that the nucleation of a new phase and its growth takes place on the surface of iron chloride crystals. The apparent activation energy (E) of the process of high-temperature hydrolysis of $FeCl_2$*$4H_2O$ in the temperature range of 603-903 K – 9.732 kJ / mol, the hydrolysis reaction of $FeCl_3$*$6H_2O$ at 503-603 K – 2.16 kJ / mol, and at 453-503 K – 5.574 kJ / mol;

– if it is necessary to obtain iron oxide powder represented by a mixture of magnetite and hematite, high-temperature hydrolysis should be performed on $FeCl_2$*$4H_2O$ crystals in the temperature range of 703-903 K and with duration of 40 minutes;

– if it is necessary to obtain a powder of iron oxides represented by hematite, high-temperature hydrolysis must be performed on $FeCl_3*6H_2O$ crystals in the temperature range of 453-603 K and with duration of 50 minutes.

Communication with other scientific research works: studies have been carried out within the framework of the Budget Program 217 “Development of Science”, subprogram 102 “Grant Financing of Scientific Research" priority “Rational Use of Natural Resources, Processing of Raw Materials and Products” on topic No. 1390/GF4 “Development of Technology for Producing Powders of Metal and Oxidized Iron of Nano-Dispersed Sizes” for 2015-2017.

The purpose of the work is substantiation and development of physicochemical bases and technology for processing solutions of iron chloride with obtaining a powder composition of ultrafine iron oxides by a chemical-metallurgical method, namely, high-temperature hydrolysis.

The objects of study are solutions of ferric chloride, obtained by etching metal rolling and leaching of iron-containing raw materials with hydrochloric acid.

The subject of research is thermodynamics, kinetics and technology of high-temperature hydrolysis of iron chloride crystals $FeCl_2*4H_2O$ and $FeCl_3*6H_2O$ obtained from iron chloride solutions, and technology of the sol-gel method to produce iron oxides, as well as comprehensive study of the composition and properties of the resulting oxide powders.

Main research tasks:

– justification of the chosen research direction;

– thermodynamic substantiation of $FeCl_2*4H_2O$ and $FeCl_3*6H_2O$ crystals high-temperature hydrolysis process;

– selection of research and analysis methods of the products obtained;

– study of the mechanism and kinetics of iron chloride high-temperature hydrolysis processes;

– study of the technological factors influence on the process of high-temperature hydrolysis;

– study of the physicochemical properties of iron oxide powders obtained by high-temperature hydrolysis and sol-gel method;

– comparative analysis of iron oxide powders obtained by different methods;

– development of the technological scheme for processing solutions of iron chloride and performing a material balance calculation;

– calculation of economic indicators of the developed technology.

Research and analysis methods:

– critical analysis and selection of research directions;

– calculation of the thermodynamic characteristics of the reactions of high-temperature hydrolysis has been performed using the thermodynamic calculation program HSC - 5.0 from OutokumpuOu;

– kinetic studies of high-temperature decomposition have been performed at the facility, using automatic titration of sodium hydroxide resulting from hydrolysis of hydrochloric acid;

– technological studies of high-temperature hydrolysis have been carried out on a facility that includes a tube furnace with a quartz reactor with a diameter of 40 mm, equipped with an automatic temperature control OMRONE5CC;

– X-ray diffraction analysis of oxide powders has been carried out on an automated diffractometer DRON-3;

– –microprobe analysis of oxide powders has been performed on an electron-probe microspectrum analyzer JCXA 733;

– thermal analysis of resulting iron oxide hydrolysis has been performed on STA-449 analyzer with a TENSOR™-27 BrukerOptics combined FTIR spectrometer and a NETZSCH differential scanning analyzer STA 409 PC PG;

– Mössbauer spectroscopy of oxide powders has been performed on a Mössbauer spectrometer Ms-1104Em;

– electronic scanning microscopy of oxide powders has been performed by using a JEOL scanning electron microscope (JSM-6610LV, Japan, 2013);

– determination of sizes and morphological features of oxidized iron powders has been carried out by using a JEOL JEM-2100F transmission electron microscope;

– determination of magnetic susceptibility of iron oxide powders has been performed by using a SatisGeoKM-7 kappameter.

Practical significance of the work is the creation of technology for processing solutions of iron chloride by high-temperature hydrolysis to produce ultra-fine powders of iron oxides of adjustable composition suitable for use in powder metallurgy. The technology is recommended for semi-industrial verification.

Provisions for the defense of a doctoral dissertation:

– substantiation of a method of processing solutions of iron chloride to produce oxides;

– results of thermodynamic analysis of high-temperature hydrolysis of $FeCl_2*4H_2O$ and $FeCl_3*6H_2O$ crystals;

– results of studying mechanism and kinetics of decomposition processes of $FeCl_2*4H_2O$ and $FeCl_3*6H_2O$;

– results of studying the influence of technological factors on the process of high-temperature hydrolysis of $FeCl_2*4H_2O$ and $FeCl_3*6H_2O$ crystals, as well as on composition and properties of resulting oxide powders;

– results of studying physicochemical properties of high-temperature hydrolysis products and a sol-gel method;

– technological scheme of processing solutions of iron chloride and the calculation of material balance.

Approbation of the work: the main provisions of the dissertation have been reported and discussed at 5 international conferences and one scientific seminar, including:

– XII Russian Annual Conference of Young Scientists and Postgraduates “Physical Chemistry and Technology of Inorganic Materials” (Moscow, 2015);

– XXVIII International Mineral Processing Congress Proceeding (Canada, 2016);

– International Satpayev readings “Scientific Heritage of Shakhmardan Esenov” (Almaty, 2016);

– XIV International Conference of the RAS Institute of Metallurgy named after A.A. Baykov “Physicochemistry and Technology of Inorganic Materials” (Moscow, 2017);

– International conference wastes: solutions, treatments and opportunities (Porto, Portugal, 2017);

– scientific seminar of the Department of Metallurgy of Non-Ferrous Metals, FSAEI of HE “Ural Federal University named after the first President of Russia B.N. Yeltsin” (Ekaterinburg, 2017).

Publications: 14 publications have been published on the topic of the thesis, including 4 articles from the list of scientific journals recommended by Committee for Control in the Sphere of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, 1 article in a foreign journal included in the Scopus database, 7 abstracts, 1 monograph published, an application have been submitted for obtaining a patent.

The structure and scope of the thesis. The structure of the dissertation includes the following elements: “Normative references”, “Designations and abbreviations”, “Introduction”, a literature review devoted to the problems of processing solutions of iron chloride, an experimental part of 5 chapters, “Conclusion”, “List of references” and “Applications”.

The first chapter of the thesis substantiates the chosen direction of research. The chapter describes the properties and applications of iron oxides powders, and methods for their preparation. The effectiveness of the use of hydrochloric acid in the hydrometallurgical processing of mattes and the etching of the iron surface has been substantiated, and the results of the exploratory research on the processing of matte that carried out to obtain the pigment composition of the powder of iron oxides are given.

The second chapter is devoted to the thermodynamic analysis of high-temperature hydrolysis reactions. Based on thermodynamic calculations of ferric chloride crystals high-temperature hydrolysis reactions in non-oxidizing and oxidizing atmospheres, the thermodynamic possibility of magnetite and hematite formation has been determined, the resulting reaction has been justified, and two mechanisms have been suggested for its occurrence.

In the third chapter, the procedures are described, and the mechanism and kinetics study results of the process of iron chlorides high-temperature hydrolysis are given. Technological parameters of temperature and duration used in the performance of technological experiments have been established by the results of the research.

The mechanism of high-temperature hydrolysis of iron chloride in an oxidizing atmosphere has been disclosed. It has been established that with the decomposition of $FeCl_2*4H_2O$ with an increase in the degree of decomposition of chloride, a change in the composition of the solid phase is observed - magnetite ratio changes: hematite - the proportion of hematite in the hydrolysis products increases. This is due to a change (decrease) in the release rate of HCl to the gas phase, which leads to an increase in the diffusion rate of oxygen of the gas phase to the reaction zone, and entails the formation of hematite together with magnetite.

The fourth chapter presents the results of technological studies of obtaining oxide powders of iron by high-temperature hydrolysis and the sol-gel method. The obtained powders have been subjected to X-ray phase analysis, microprobe analysis, differential scanning calorimetry, Mössbauer spectroscopy, scanning and transmission electron microscopy, and the magnetic susceptibility of the powders has been determined. It has been established that the finest powder (particle size of 20–40 nm) is obtained by high-temperature hydrolysis of $FeCl_2*4H_2O$ at a temperature of 903 K, the technology for the preparation of which is recommended for semi-industrial testing. As a reactor for carrying out the process, a “fluidized bed” furnace is recommended.

On the basis of the studies performed in the fifth chapter a schematic process flow diagram has been developed by using the process of high-temperature hydrolysis of iron chloride, and material balance calculations have been performed.

The sixth chapter presents an approximate economic calculation, which shows that the profitability of the developed technology is 35%. The cost of 1 kg of nano-dispersed iron oxide powder is $ 4 US with a market price of $ 5-6 / kg.