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PROSPECTS FOR THE EXTRACTION OF CHROMIUM FROM SLAG FERROCHROME PRODUCTION BY ACID METHOD

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Abstract: Introduction. In the Republic of Kazakhstan, there is a noticeable upward trend in the volume of industrial waste, including from the production of ferrochrome. The problems of man-made pollution of the natural environment are becoming more acute every year, and are beginning to take on a global dimension. Technogenic ferrochrome production waste contains chromium, which is highly toxic and carcinogenic, which poisons water, soil, negatively affects the activity of all living organisms. Slags contain a significant number of valuable components used in various industries, and above all, chromium. which is irrevocably lost during storage. The main task still remains the development of industrial waste disposal processes that reduce the anthropogenic load on the biosphere and ensure the rational use of natural resources. The purpose of the work is to justify the choice of the method of processing the slags of the ferrochrome production. Conclusions: The analysis of the modern scientific and patent literature on acid processing and utilization of chromium-containing slags from the production of refined and highcarbon ferrochrome has been conducted. It should be noted that the described methods of various methods of processing ferrochrome production slags, despite their availability, are characterized by a multi-stage nature and do not allow complete processing of ferrochrome production slags in Kazakhstan. Currently, there is an excess of sulfuric acid production in Kazakhstan, so it becomes advisable to use sulfuric acid as a reagent for leaching chromium from slag from the production of ferrochromium. It can be expected that in sulfuric acid under certain conditions, such as heating, a sufficiently high degree of extraction of chromium (III) will be achieved in slags from the production of high-carbon chromium and in refined ferrochem slags.

Keywords: ferrochrome production, chromium-containing slags, leaching, slag separation, sulphuric acid, hexavalent chromium, trivalent chromium.

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1. Introduction

In the Republic of Kazakhstan, there is a noticeable upward trend in the volume of industrial waste, including from the production of ferrochrome [1]. At present, the problems of man-made pollution of the natural environment are becoming more acute every year, and are beginning to take on a global dimension.

Technogenic ferrochrome production waste contains chromium, which is highly toxic and carcinogenic, which poisons water, soil, negatively affects the activity of all living organisms [2-5]. Only about 20% of the waste is recycled and reused. Waste is usually located in special landfills of the industry itself and, despite the measures taken to store it safely, pollutes the environment. In this regard, the recycling and utilization of industrial waste is highly relevant, not only contributing to the reduction of pollution, but can also be an element of resourcesaving technologies. Among the solid, liquid and gaseous wastes from various industries, the ferroalloy slags deserve attention. Slags contain a significant number of valuable components used in various industries, and above all, chromium, which is irrevocably lost during storage.

Chromium can accumulate in the biosphere and living organisms.

The main pathway for the release of chromium into the environment is through the production of chromium and its compounds from chromium ore and its further processing. Industrial waste from these enterprises plays an important role [2, 3].The development of the industrial waste management processes that reduce anthropogenic pressures on the biosphere and ensure the sustainable use of natural resources remains a major challenge [4]. So in [6] it is noted that the MPC of chromium for plants is from 0.1 to 2.0 mg/kg of dry mass, and the critical mass of the metal varies from 1.0 to 2.0 mg/kg of dry mass, above which the increase in the above-ground mass of plants is reduced by 10%. The high concentration of chromium in plants significantly inhibits all growth processes and causes plant disease. Chromium content is particularly increasing in plants growing in ore deposits, terricons, as well as in areas contaminated by this element.

Chromium is present in both vegetable and outgoing food products in the form of inorganic salts, as well as in the form of a complex compound with organic ligands, which is a biologically active form of chromium with a pronounced presence of carbohydrate metabolism [2]. Higher frequencies of chromium are observed in fish, milk, dairy products, meat of domestic animals.

With food, chromium absorbs the human body and affects it. Chromium is an increased stimulant and causative agent of cancer, pulmonary and cardiovascular and other diseases, increased consumption for accumulation in food chains, and their sustainable risk to humans [2-7]. Aktobe region alone accumulated at least 830 mln. tons of industrial waste, of which 12-15 mln. tons are slag waste. Moreover, more than 5 million tons are represented by slags from the production of high-carbon ferrochrome and more than 8 mln. tons - pulverized, low-carbon ferrochrome slag [8]. According to [9] data in Aktobe region, contamination of soil, water and air with hexavalent chromium is recorded with a significant exceedance of the MPC until 2010. However, in the period from 2011 to 2015 there is a positive trend of its decrease by 10-thousandths shares, which is due to the involvement in the processing of ferrochrome slags stored at the range [10-14]. Therefore, there is a need for more intensive involvement in the processing of chrome-containing slags.

2. Chemical and phase composition of ferrochrome slags

Ferrochrome slags are characterized by a high content of magnesium oxide (MgO), the amount of which varies between (7.0-45%) [15,16]. The chemical and material composition of ferrochrome slags is not constant and depends on the quality of the raw material used and the variety of ferrochrome produced [17-19].

The refined ferrochrome slag (RFC) slag of JSC "Aktobe Ferroalloy plant" used in work [15] has high content of Cr_2O_3 (15.11 %) and FeO (4.08 %). Their content is 2.52 and 2.04 times higher, respectively, compared to Cr_2O_3 and FeO in RFC slag, the composition of which is given [17]. The oxides Mg, Al, Si and Ca in the RFC slag sample according to the data presented in the work [15] are 4.0, 2.11, 2.0 and 7.7% lower than the RFC slag sample used in Article [17].

Slags from smelting of high-carbon ferrochrome at the Serov Ferroalloy Plant, Chelyabinsk Electrometallurgical Plant are refractory material, the main mineral phases of which are forsterite (55-60%), aluminomagnesial spinel (36%)glassy phase of the mellithic composition (3-4%) [19]. In other samples, there may be less forsterite, because ferrochromic slags are characterized by the variability of the composition of the composition. The refined ferrochrome of AktobeFerroalloy plant contains 33.2%, its full phase composition (weight. %: 33.2 Mg₂(SiO₄); 22.5 MgFeAlO₄; 20.5 Ca₃(SiO₄), 2.S;7.9 AliOSO₆; 6.5 MgFeO₄; 20.5. Mg₂SiO₄ and MgAl₂O₄ are present in the high-carbon ferrochrome slag, and Mg₂SiO₄orthosilicate (forsterite) is present in the low-carbon ferrochrome slag, orthosilicalcation in the form of a modification y-Ca₂SiO₄ and partially as a-Ca₂SiO [20-22].

High-carbon ferrochrome slag is used as a roadblock [23], while low-carbon ferrochrome slag is only used. In 2019, ERG Recycling started to implement a program for the processing of laid slags from the smelting of the ferroalloys of TNC «Kazchrom» (RK) for 2019-2021. [24, 25]. In the same year, 50,000 tons of

these wastes were recycled to produce chrome metal concentrate and slag inert materials. In 2019-2020, slag and slag sand were tested in road construction and as concrete filler in 2020. Certificates of conformity for this type of product have been obtained [26]. It should be noted that the processing of slags from the production of refined ferrochrome is very difficult and most of them are in piles and worsen the ecological situation of the region, for example in Aktobe region [13]. Lower oxidation chromium compounds are not poisonous, but in the body they can change to Cr (VI) [27, 28].

The problem of processing waste slags and extracting metal components from them, and then using them as the secondary raw material is one of the most important in metallurgy. The issue is being addressed from the perspective of zero waste technologies. The basis of such technologies is the development and introduction of fundamentally new technological processes, excluding all types of waste, various non-recurrent technological schemes and water recycling cycles on the basis of effective cleaning methods, as well as the widespread use of waste as a secondary raw material.

Methods of processing ferroalloy slags are very diverse (air and magnetic separation, slag stabilization, metallurgical processing, mechanical grinding, leaching, hydrothermal processing, etc.) [15, 29-31], their choice is determined by the features of slag, and economic and environmental feasibility.

3. Slag separation

Screening with subsequent magnetic separation of metal elements is suitable for RFC slags; alloy pellets are separated from this slag by air or magnetic separation [32]. This method effectively uses magnetic separation to increase the [Cr:Fe] ratio in fine ferrous chromite.

In the method [33] for extracting metal concentrate from chromiumcontaining slag, the crushed material is fed to the conveyor and the metal concentrate is taken in the form of a magnetic fraction using a pulley under the action of a magnetic field created by magnets. In this case, the non-magnetic fraction is first removed, and then the magnetic fraction is removed with a knife, which is pressed against the conveyor belt by the magnetic field of the pulley. Moreover, manual sampling of the metal concentrate is carried out.

In the method for processing low-carbon ferrochrome slags [34] after rattling the raw material for 10-15 min the slag is treated in an air cooling stream at a speed of 4 m/s. Then the slag passes through an air separation to a fraction of 20 mm in an upward flow at a flow rate of 10 m/s with mixing the material in a suspended state to a temperature of 0-60°C. Then the slag powder of the 0.4 mm fraction (dust removal) is separated from the slag. Both products then pass the magnetic two-stage stage for metal extraction. However, there is a residual metal content in a non-magnetic product.

The metal (chromium) can be separated from the mineral part of the slag by pneumatic separation and sifting on the sieves, and the mineral part of the slag is efficiently processed by mixing it with the ferrous Kazakhstani diatomite (flask)liquid glass and thermal treatment of granules to produce a porous glass insulating material [16].

Another option is to combine pneumatic separation with magnetic separation. This technology may work, but its performance is significantly limited [20.32]. The main limitation is the humidity of both the feedstock (up to 5%) and the ambient air. Drying the waste before separation is not economically profitable.

According to the method [35], the ferromagnetic inclusions of the dust particles (0-0.3 mm) are extracted by the magnetic air separator incorporated into the dust capture system. The magnetic products extracted at all stages of the processing of the slag are purified by breaking the bonds holding the inclusion of the slag on the metal product in an impact crusher with subsequent magnetic separation.

The object of the invention [36] is chromium-containing ferroalloys, in particular slags, dust and other wastes. The original slag was subjected to stagal crushing, with the crushing products being divided into size classes. Then separated by methods of magnetic and gravitational enrichment. Grinding, classification and separation were carried out in both dry and wet ways. As a result, a chromium-containing concentrate and a calcium-containing magnesium-containing product are released, the latter can be used in the manufacture of refractory materials. The defects are multi-layered and chromium loss ranges from 26 to 14%.

The method for extracting chromite concentrate from waste materials for processing chrysotile-asbestos ores comprises a preliminary granulometric separation, a separation of a fine product, from which the separation of the magnetite concentrate is obtained by gravity method of heavy fraction and further by magnetic separation. A chromite concentrate [37] is extracted from the waste produced by electromagnetic separation.

The invention [38] is intended for processing slags from the production of high-carbon ferrochrome grades and can be used for extracting low-magnetic alloys from metallurgical slags. The first stage of magnetic separation is carried out at the induction of a magnetic field of 120-200 μ T with the release of a magnetic product, and the non-magnetic product of the first stage is subjected to magnetic separation at the second stage in one or two receptions at the induction of a magnetic field of 300-1000 μ T. Due to optimization of the parameters of the extraction process was 92.8%.

The method for processing carbon ferrochrome slag [39, 40] involves crushing the slag, splitting the crushed slag by ratcheting at a margin of 3-5 mm, pneumatic classification and magnetic separation of separation products. As a result of the processing of metallurgical slags, several commercial products are obtained - a metal concentrate and slag products used as abrasive and refractory materials. In this process, the carbonaceous ferrochromium slag meets the requirements of a forsterite spinel product.

Employees of Gravikon Company have developed the technology of enrichment of HCFC slags formed at JSC «Kazchrom» by hydraulic removal [41]. The result is pure commercial ferrochrome and industrial product, which was sent to the melting, as well as chromium-free rubble. The latter is used in road construction.

The options for the technology of separating lumpy materials using radiometric and other methods seem to be promising [42]. X-ray radiometric separation (RRS) refers to "dry" and "direct" methods for lumpy separation, literally "sees" those elements that make up valuable and associated minerals. The material composition of almost all types of slags of this enterprise allows for a clear separation by the measuring system of the separator (according to X-ray spectra).

To obtain a metal-rich concentrate, it is advisable to use a two-stage live magnetic separation. The use of the silicate base of such slags in metallurgical production is impractical due to the increased silica content, the presence of extraneous impurities and the low concentration of leading elements [43].

The described methods of air, magnetic and pneumatic separation, gravity, hydraulic removal and radiometric enrichment, chrome-containing slags have advantages and disadvantages. For example, wet magnetic separation complicates the process, the efficiency of magnetic and air separation of low-carbon ferrochrome high-carbon slag [44]. The gravitational technology of chromium ore enrichment allows the production of chromium concentrate from large and medium fractions, and fine sludge is practically not enriched due to the difficulty of separating complex minerals into chrome concentrates and waste [45]. At the same time, in all methods there are significant losses of main products with dust-like fractions.

4. Slag stabilization

The most promising outlook is borate slag [14]. Thus, the stabilization of the 2CaO•SiO structure, in particular, the mineral belite present in ferrochromic slag turns into a slag ladle with the formation of its unloading and crushing when the melt is cooled [30]. The stabilized slag is completely crystallized, has a fine-grained structure, and consists mainly of larger block grains of larnite interspersed with fine and rare grains of spinel and periclase. Slag-like larnite of increased reaction rate with water, which expands the range of slag use [19].

5. Thermal method

The melting method relates to methods of radical neutralization of chromium-containing raw materials. It is a hexavalent chromium decontamination process under high temperature conditions with the addition of an auxiliary agent [45]. The technology for neutralizing chromium slag by the melting method includes the coal-reduction method, melting in a cyclone furnace and agglomeration.

The agglomeration decontamination of chrome slag is performed using existing equipment at the metallurgical plant and is a by-product of the production process. This technology includes two stages of the process. First stage -

agglomeration, after agglomeration chromium slag is melted to produce chromium-containing product - second stage [46]. In the first stage, under the action of the high temperature of the agglomeration, Cr^{+6} passes into Cr^{+3} , i.e. the process of chromium reduction takes place, thereby neutralizing the chrome slag.

In the invention [47] a charge for producing a high-carbon ferrochrome is prepared by metering a carbon reducing agent, a high-carbon ferrochrome production waste, a low-carbon ferrochrome slag held in a pile and a chrome ore. Breaking down the silica slag barrier contributes to chromium recovery from chrome spinelide chromium ore with coke carbon and CO gas.

The molten slag produced during the production of carbon ferrochrome in the ore thermal furnace is provided with a slag obtained from the smelting of refined ferrochrome in the amount of 50-120% [48]. The inventive low-melt slag melt is produced with a melting point of I650-I700°C. The process of chrome splitting and chromium reduction is facilitated by the introduction of aluminium into the melt, in the amount of 2-10% of the slag weight.

The aim of the invention [49] is to extract chromium oxides from the slag formed after the process of melting a chrome-containing slag in an electric arc furnace. The main disadvantage of thermal methods is high energy consumption due to the use of high temperatures and the need to neutralize the resulting flue gases.

6. Hydrometallurgical method

The method is based on hydrometallurgical leaching and sorption technologies. Can be used in chromite ore mining and chromium compound production. It allows to recycle highly toxic chromium VI compounds from waste products of different physico-chemical condition with the release of chromium into a high purity commercial product (content of Cr_2O_3 not less than 95%). It drastically reduces the amount of hexavalent chromium emitted into the environment by the chrome industry. Allows you to gain additional profit by returning chromium to the commercial product.

The method [50] for obtaining chromite concentrate from poor chromiumcontaining ore provides for grinding the ore to a particle size of less than 2 mm, roasting at 500-550°C for 2 hours. The roasted ore is further leached by treating it with mineral acids (sulphuric H2SO4 or hydrochloric HCl) in two stages. Disadvantages of the method: multi-stage process, the need for pre-calcination of serpentine ore, heating of acid leaching solutions used in the second stage, as well as a caustic soda solution used to process the cake. In addition, the concentration of chromium in leaching solutions and the frequency of return of acid solutions for leaching are not indicated. There are no data on the disposal of waste solutions.

A known method for enriching chromite ore involves thermochemical and hydrometallurgical processing of ore containing as an impurity of olivine, from which white magnesia is obtained by hydrometallurgical methods [51]. This method makes it possible to involve poor, substandard ores in processing, but differs by the high cost of thermochemical treatment of the entire volume of ore, because its roasting is carried out at 600°C within 1 hour. In addition, the filtrate obtained by hydrochloric acid leaching of burnt ore undergoes thermal hydrolysis.

The essence of the invention [52] consists in the treatment of chromium production sludge with uterine solutions produced after the basic magnesium carbonate. The composition of the produced slurry (8.33-8.52% MgO; 0.32-0.40% CrO₃; 33.0% CaO; 6.33-6.40% Cr₂O₃) allows it to be used in a non-colomittal chromatic production process or in a composition for cement production.

In the [53] method, the aqueous suspension of chromate-produced sludge is treated with sulfuric acid with a concentration of 190-200 g/dm³. The result is chromium oxide and a magnesium-enriched solution. In this method, the difficulty lies in the hardware design, in particular the need to use an autoclave.

The work [52] proposes a method for hydrometallurgical processing of ferrochrome production waste by sulfur acid leaching in order to produce chromium concentrate (Cr_2O_3) and magnesium sulfate solution (MgSO₄). This method allows the recovery of valuable metallurgical constituents from waste for further processing. Studies were carried out on chromium drift dust from the furnace 41 Pz-4 JSC "Aktobe Ferroalloy plant", caught wet gas cleaning, wet (hydrometallurgical) leaching solutions of mineral acids and ammonium hydrosulphate.

Currently, the deposition of chromium hydroxide from sulphate solutions containing trivalent chromium is produced with iron vitriol and calcareous milk. The method [53] proposes the deposition of chromium-oxide lead with the addition of two-calcium silicate produced by calcification.

It should be noted that a significant part of the work is aimed at processing (neutralizing) mainly chromium-based sludge, including the toxicity of hexavalent chromium sludge from this production. The proposed solutions involve the use of inorganic salts or sulphur, elevated temperatures, or the process in the autoclave. Hydrothermal processing of chromium production waste is also carried out by mineral acid at elevated temperatures and is characterized by multi-stage.

7. Leaching

To extract chromium from solid chromium-containing waste, a leaching method is used using solutions of alkalis, acids and salts.

An analysis of the scientific literature showed that the method of alkaline and acid leaching is at the stage of exploratory research. So in [54], the extraction of chromium from sludge (dumps) of chromate production is carried out with a 30% solution of sodium hydroxide NaOH and a 10% solution of hydrochloric acid. Consumption experiments at ambient temperature (22°C), change over 30 min. The chromium content in the hydrochloric acid leaching solution is 2290 mg/l higher than in the sodium hydroxide solution.

The method of alkaline and acid leaching is also used to extract chromium from sludge from the neutralization of waste solutions after treating the surface of the skin [55]. Sludge from HPC-3 "ArcelorMittal Temirtau" was leached with solutions of NaOH, KOH, NH₄OH of various concentrations. For the acid removal of chromium, H₂SO₄, HNO₃, HCl, H₃PO₄, as well as a mixture of acids were detained. The lowest degree of chromium recovery from chromium-containing sludge (71.0%) obtained by alkaline leaching. Acid leaching is more efficient. In acid leaching of chromium-containing sludge, the best result was obtained for a sulfuric acid solution.

The authors of [56-58] as a promising isolation of chromium compounds from aqueous chromium-containing solutions are investigating the ozonation method. Ozonation, or developing oxidation processes (using ozone decomposition products as oxidizing agents), are widely used in industrial wastewater and drinking water treatment plants, food products, that hydroxyl radicals are formed during ozone decomposition, and oxidizing agents are also found [56, 57]. Studies [57, 58] consider the possibility of using ozone suspension of chromite ore or slag from ferrochrome production to convert trivalent chromium to hexavalent. Ozone degradation by-products have also been shown to be strong oxidizers in South African chromium ores ozone depletion and the use of ozone ozone neutralization for South African chrome ores is an effective method [58]. In the same paper, the oxidation process of trivalent chromium contained in chromite ore or slag from ferrochrome production into hexavalent is highlighted. Influence on the degree of oxidation of chromium dispersion and the type of source material, liquid phase pH, temperature and time of treatment by ozone suspension has been determined. However, due to the limited capacity of the ozone emitter, the maximum oxidation of chromium was 15%.

In [59], the sludge (dump) of chromate production was leached with water with simultaneous treatment of the suspension with ozone at a sludge: H_2O ratio of 1:20 for 30 and 45 min. As a result of the work carried out, the fundamental possibility of using ozonation to increase the degree of chromium extraction during aqueous leaching of chromate production sludge is shown. A tendency towards an increase in the chromium content in sludge fractions characterized by large particle sizes, i.e. preliminary grinding of raw materials is necessary.

A comparative analysis of the processes of extraction of chromium from chromium-containing sludge by alkaline and acid methods showed that the efficiency of acid leaching is higher. Moreover, when using alkalis, difficulties arise with the regeneration of solvents and their disposal. In this regard, attention should be paid to the study of the method of acid leaching.

The article considers [60] the possibility of processing chromate sludge from the Aktobe plant of chromium compounds for magnesium oxide, using sulfamic acid. The choice of sulfamic acid was due to its low toxicity, good solubility of sulfamates of many metals, low corrosivity, and the possibility of carrying out the leaching process at ordinary temperature in reactors without acid-resistant lining. The authors of this article showed the possibility of using sulfamic acid for leaching MgO from chromate sludge with further production of commercial products based on it and found that chromium does not adversely affect the magnesium leaching process.

An interesting work [61], in which it is proposed to carry out sulfuric acid leaching of chromium-containing galvanic sludge in one stage with a 10-15% solution of H_2SO_4 at a ratio of S:L = 1:3 (for wet sludge) at a temperature of 30-40°C for 1.5 h at mixing. After sedimentation and filtration using flocculants, the leaching solution with pH 1 is sent to the sorption filter. The precipitate after washing is filtered on a press or vacuum filter and sent to a disposal site for use as an additive in the manufacture of ceramic tiles or other building materials. According to the developed technology, the following indicators were obtained: Cr extraction was 81.2%, Ni - 93.5%, Zn - 97.5%, Cu - 82.1%.

In [62], sulfuric acid was chosen as the leaching agent, which was due to the chemical properties of the extracted element [63]. The leaching process was carried out in an agitator under various conditions: changing the pH in the range of 0-12, different stirring speeds and temperatures. X-ray phase analysis of sediments isolated after slag leaching revealed the presence of silicon and chromium, the ratio of which in terms of oxides was 2:3, respectively. This study is an intermediate stage of work aimed at obtaining a concentrate with a high chromium content from chromium-containing slag.

When processing technogenic chrome-containing waste combined methods are used.

In the work [64] the process of production of magnesium oxide from the chromium-containing raw material of the deposit of Kazakhstan with preliminary production of chromium oxide (VI) is investigated. The study also uses concentrated sulfuric acid.

It should be noted that the information on acid leaching of chromium slag in the scientific literature is limited and mainly of a search nature.

The work [65] offers the technology of complex processing of nontraditional raw materials - serpentine and serpentine waste heaps on chrysotileasbestos and chromite deposits. The method involves grinding the ore, heat treatment, leaching with solutions of mineral acids with subsequent filtration of the suspension, washing and drying the end product. The heat treatment is carried out at the temperature of 500-550°C, and the leaching and filtration process is carried out in two stages with an additional treatment of the solid residue with a solution of caustic soda with the subsequent filtration. Furthermore, the first step of leaching consists in treating the burned ore with acid recycled leachate with the concentration of 230-250 sulfuric or 90-110 g/l hydrochloric acid, with subsequent filtration of the suspension and directing the solid residue with a solution of sulphuric or hydrochloric acid concentration, respectively, 300-550 and 110-220 g/l with subsequent filtration of the suspension and the direction of the leachate to the first stage of leaching.

In the method [66] it is proposed to process the slag in order to produce a chromium-containing concentrate and a magnesium-enriched solution. However,

this process is carried out in the autoclave at 110-160°C, using aggressive sulfuric acid. The invention relates to processing the slag wastes formed during the enrichment of chromite ores to produce a rich slurry corresponding in terms of chromium oxide content to a chromium concentrate, separated by chromium oxide and magnesium and concentrated in the solution. The processing of chromate production slag involves treating the aqueous slurry thereof with sulphuric acid, separating the magnesium sulfate solution from the solid phase (slurry), wherein the slurry tails are treated in the autoclave at the temperature of 110-160°C, and the initial sulphuric acid concentration of 190-C acid 200 g/dm³, autoclave pressure 0.15-0.7 MPa, leaching time 2-3 hours with active agitation by mechanical mixer with 150-250 revolutions per minute. Furthermore, the sludge is additionally treated with ammonium carbonate (NH₄)₂CO₂ in a quantity of 10-20% of the slag mass. It should be noted that a significant part of the work is aimed at processing (neutralizing) the slag, including the toxicity of slag containing hexavalent chromium, of current production. Most of the proposed solutions are related to high-temperature processes [67,68] using sufficiently aggressive reagents such as mineral acids [69-71].

In the [72] method, the acid leaching method is used for extracting chromium from ores. The process is carried out by mixing chromite ore with manganese raw material containing manganese dioxide, grinding the mixture with the introduction of concentrated sulfuric acid. The ratio of chromite ore to manganese and sulfuric acid varies from 1:1:1 to 1:2:10. The mixture is heated at the temperature of 200-500°C, then cooled in air and then leached with water at the temperature of 60°C for 3 hours. The solution after leaching is treated with an organic solvent or ion exchange resin for chromium extraction. Manganese is extracted from the aqueous phase. Amines are used as an organic solvent and anion exchange resin is used as an ion exchange resin. The process is carried out at the elevated temperatures, concentrated sulfuric acid and organic substances are used and are characterized by a multi-stage character.

The process of production of magnesium oxide from chromium-containing raw material of one of the deposits of Kazakhstan [73] has been investigated. In this study, raw materials have been processed: the particle size of the original ore has been taken up to 20 mm, after mechanization the particle size has changed to 0.5 mm. Then the ore has been subjected to the "wet" magnetic separation. The next stage is the leaching of sulfuric at different concentrations of the non-magnetic fraction with and without heating. The stage has been carried out with intensive mechanical mixing (5 rev/sec) [74]. An initial filtration with the separation of the slag has been carried out. Chromium oxide (VI) is present in the solid sediment. During the fractional deposition process, the target product has been obtained with a purity of 99.5%. The remaining solution has been mixed with soda (GOST 5100-85) until full deposition. The reaction mass has been filtered, the sediment has been dried at the temperature of 180 C. During chemical transformations and technological operations, magnesium oxide has been obtained with a purity of 98.2%.

The main activity of "Voskhod-Oriel" LLP is carrying out works on development of "Sunrise"chrome ore deposit [75]. The "Voskhod" chrome ore deposit is located in the Khromtau district of the Aktobe region. At the moment the object of expansion of the area of the rock heap according to the project "Expansion of the rock heap TO-17-08" is the existing rock heap of empty rocks at the "Sunrise" deposit. In order to reduce waste it is proposed by "Voskhod– Oriel" LLP to process slag waste, generated by processing chromite ores with the production of rich sludge, the chromium oxide content corresponds to chromite concentrate with chromium oxide and magnesium separation and magnesium concentration in solution.

The known method for processing chromatic slag consists in restoring the hexavalent chromium, contained therein, to a trivalent state by treating aqueous sludge slurries with sulfur-containing reducing agents in an alkaline medium at the temperature of 122-160°C [76].

The work [77] has investigated the possibility of recovering hexavalent chromium with the traditional and alternative reagents. A mathematical model of the hexavalent chromium recovery process has been built. This work has investigated the recovery of hexavalent chromium, using traditional and alternative reagents. The subject of the study has been model run-off with a chromium ion (VI) concentration of 600 mg/dm³.

As a result, a mathematical model approximating the process of changing the concentration of chromium (III) and chromium (VI) ions during the recovery process has been obtained by an experimental method. The most effective reducing agent at a minimum amount of reagent is sodium sulfite. The least effective are iron turnings, aspen sawdust and conifer sawdust with a degree of purification of hexavalent chromium ions 98, 75 and 83%, respectively. Despite the above, the use of these reagents is an alternative, as they are waste products of the production.

When studying various physical phenomena and conducting technological experiments, a functional relationship is often observed between quantities that describe the quantitative side of a given phenomenon or experiment. To show this dependence, sometimes it is necessary to carry out a huge number of experiments. This requires a lot of time and a large number of reagents. In connection with the foregoing, in this work, for mathematical processing of the results of experimental studies, following the work [78,79], the interpolation method [80] has been used.

In this paper, the possibility of using traditional and alternative reagents for chromium ion reduction (VI) has beenstaudied. It has been shown that the sharing of traditional and alternative reagents is the most affordable, cheapest and quite effective method. A mathematical model of the hexavalent chromium recovery process has been built. In particular, a functional dependence approximating the results of the experimental studies has been established (the confidence value of the approximation is 0.99).

The work [81] has examined the possibility of extracting magnesium oxide from the toxic waste from the production of chromium salts - chromium

slaghydrochemical method, using sulfamic acid. In the studies the method of probabilistic-deterministic planning of experiment, developed in the Karaganda Chemical-Metallurgical Institute has been applied. Mathematical models of extraction of magnesium oxide into products of chromium slurry leaching have been found. Optimal conditions of the leaching process have been determined. The proposed method for solving the problem of extraction of magnesium from the waste materials of the production of chromium compounds using a non-toxic leaching reagent is novel.

The work [82] shows that slag disposal can be organized so as to result in not only building materials, but also metal suitable for further processing and use. For the thermodynamic modeling of processes during the recovery of slag piles, the software complex FactSage (version 6.4) has been used. Slag reduction has been simulated for three different FeO formulations (15, 10 and 5% (by mass)). The simulation is performed in the temperature range of 750 - 1650C in 5°C at the gas phase pressure of 0.1 MPa. The model assumed that a known excess of carbon had been introduced into the system as a reducing agent. Model results clearly indicate that carbon monoxide will dominate the gas phase over the whole temperature range considered.

It should be noted that the production of chromium in Kazakhstan is expanding, we can expect an increase in the volumes of technogenic chromecontaining wastes. And despite the fact that ERG Recycling, a part of TNK "Kazchrom" JSC, in 2021 will recycle 150 thousand tons of waste and by 2025 will it will achieve the annual volume of chrome-containing waste processing 500 thousand tons [83]. A significant amount of slag, sludge and other chromecontaining wastes will still be in the tailing heaps. Therefore, the further development of processing the chromium-containing slags is needed. An analysis of the scientific and patent literature has revealed that acceptable methods of processing chrome-containing slags include enrichment methods. However, a number of factors need to be taken into account when choosing how to process chrome-containing slags. For example, the availability and affordability of the used reagent for processing chrome-containing slags, their mineral composition, the processability of the method, the possibility of the further use of the processed slags, etc.

According to the data given in the article [9, 84], the mineral composition of the slag from the production of high-carbon ferrochromium is mainly represented by forsterite Mg_2SiO_4 , spinel $MgAl_2O_4$, and a partially amorphous glassy phase. In the slag from the production of low-carbon ferrochrome, the main crystalline phase is calcium orthosilicate γ -Ca₂SiO₄, as well as magnesium orthosilicate (forsterite) Mg_2SiO_4 [85]. The authors of the studies [85, 86] have found that from the point of view of chemical, mineralogical composition and refractoriness, the slags from the production of high-carbon ferrochrome and low-carbon ferrochrome can be a valuable raw material for the manufacture of heat-resistant materials.

In [87], the mineral part of the slag after chromium leaching has been used to obtain on its basis a granular porous glassy filler material for heat-concrete products with low thermal conductivity.

In [88], high-carbonferrochromium slag has been used for road construction. Coarse fractions of slag are used as a coarse aggregate for road construction, since they have a module Mk = 2.9 and meet the requirements of GOST 3344-83 "Crushed stone and slag sand for road construction." The use of small fractions (less than 5 mm) of this slag, formed during slag crushing, as a filler for road construction has shown that the strength of the studied standard samples is on average 1.5 times higher than the strength of control samples prepared using granite screenings and the Volsk sand.

The available developments in the processing of slag ferrochrome are mainly related to the use of elevated temperatures (40-90°C) and different concentration acid solutions [89]. More promising is the extraction of chromium in the sulphuric acid process of ferrochrome slag processing, with the further extraction from the residues of safe building materials.

It should be noted that there is currently an excess production of sulfuric acid in Kazakhstan [90]. That is, sulphuric acid can be used as a reagent for leaching chromium from the production of ferrochrome. This ensures that they are defused. For example, heating will achieve a sufficiently high degree of extraction of chromium (III) in slags from the production of high-carbon chromium and in refined ferrochem slags.

Therefore, the acid way of leaching them becomes attractive. According to [87,88,91], low-carbon slags, including slags from the refined ferrochrome production, contain Cr (VI), which will be converted into sulfuric acid leaching solution. Hexavalent chromium in the sulfuric acid solution of slag leaching from RFX production must be subjected to acid reduction to harmless trivalent Cr. A method for reducing hexavalent chromium into trivalent form using reducing reagents and deposition of trivalent chromium in the form of hydroxide [92] is widely used. However, the adsorption methods for cleaning solutions, containing chromium, including Cr^{+6} [93, 94], are now becoming relevant. Natural aluminosilicates can be used as available, cheap sorbents [95].

The mineral part of ferrochrome slags after leaching can be used to produce road building materials in which the leached mineral part of slags can be the basis for producing compositions with adjustable gypsum content.

8. Rationale for the choice of a method for processing slag from the production of ferrochromium

It should be noted that the described methods, despite their availability, are characterized by a multi-stage nature and do not allow complete processing of ferrochrome production slags in Kazakhstan [16]. An analysis of the scientific patent literature revealed that enrichment methods are acceptable methods for processing chromium-containing slags. However, when choosing a method for processing chromium-containing slags, a number of factors must be taken into account. For example, the availability and cheapness of the reagent used for the processing of chromium-containing slags, their mineral composition, the manufacturability of the method, the possibility of further use of processed slags, etc.

According to the data given in [95], the mineral composition of high-carbon ferrochromium production slag is mainly represented by Mg2SiO4 forsterite, MgAl₂O₄ spinel, and partially amorphous glassy phase. In the slag from the production of low-carbon ferrochrome, the main crystalline phase is calcium orthosilicate γ -Ca2SiO4, as well as magnesium orthosilicate (forsterite) Mg2SiO4 [25]. The authors of studies [25, 96] found that, from the point of view of the chemical, mineralogical composition, and refractoriness, slags from the production of high-carbon ferrochrome and low-carbon ferrochrome can be a valuable raw material for the manufacture of heat-resistant materials.

It should be noted that currently in Kazakhstan there is an excess production of sulfuric acid [97]. Sulfuric acid can be used as a reagent for leaching chromium from slag from the production of ferrochromium. According to [16, 22, 26, 98], low-carbon slags, including slags from the production of refined ferrochromium, contain Cr (VI), which will pass into the sulfuric acid leaching solution. Hexavalent chromium in the sulfuric acid leaching solution of slags from RHF production must be subjected to acid reduction to harmless trivalent Cr. The method of reduction of hexavalent chromium to the trivalent form with the use of reducing agents and the precipitation of trivalent chromium in the form of hydroxide is widely used Natural aluminosilicates can be used as affordable, cheap sorbents [99,100].

The mineral part of ferrochromium slag after leaching can be used to produce road building materials, in which the leached mineral part of the slag can be the basis for obtaining composite compositions with a controlled gypsum content.

Conclusions.

The analysis of modern scientific and patent literature on the processing and disposal of chromium-containing slags from the production of refined and highcarbon ferrochrome has been carried out. It should be noted that the described methods of various methods of processing ferrochrome production slags, despite their availability, are characterized by a multi-stage nature and do not allow complete processing of ferrochrome production slags in Kazakhstan. Currently, there is an excess of sulfuric acid production in Kazakhstan, so it becomes advisable to use sulfuric acid as a reagent for leaching chromium from slag from the production of ferrochromium. This achieves their neutralization. It can be expected that in sulfuric acid under certain conditions, such as heating, a sufficiently high degree of extraction of chromium (III) will be achieved in slags from the production of high-carbon chromium and in refined ferrochem slags. Acknowledgments: This work was funded by the Committee of Sciences of the Ministry of Sciences and Higher Education of the Republic of Kazakhstan (Grant No. BR18574042, "Innovative methods of synthesis and technologies for obtaining functional inorganic and organic substances and materials from natural and technogenic raw materials").

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ПЕРСПЕКТИВЫ ИЗВЛЕЧЕНИЯ ХРОМА ИЗ ШЛАКОВ ПРОИЗВОДСТВА ФЕРРОХРОМА КИСЛОТНЫМ СПОСОБОМ

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Резюме. Введение. В Республике Казахстан наблюдается заметная тенденция к увеличению объемов промышленных отходов, в том числе от производства феррохрома. Проблемы техногенного загрязнения природной среды с каждым годом обостряются и начинают приобретать масштабы. техногенного произволства феррохрома глобальные Отходы содержат высокотоксичный и канцерогенный хром, отравляющий волу, почву, негативно влияющий на жизнедеятельность всех живых организмов. Шлаки содержат значительное количество ценных компонентов, используемых в различных отраслях промышленности, и прежде всего, хром, безвозвратно теряющийся при хранении. Главной задачей по-прежнему остается разработка процессов утилизации промышленных отходов, снижающих антропогенную нагрузку на биосферу и обеспечивающих рациональное использование природных ресурсов. Цель работы - обосновать выбор способа переработки шлаков феррохромового производства. Выводы: Проведен анализ современной научной и патентной литературы по кислотной обработке и утилизации хромсодержащих шлаков производства рафинированного и высокоуглеродистого феррохрома. Следует отметить, что описанные способы различных способов переработки шлаков производства феррохрома, несмотря на их доступность, характеризуются многостадийностью и не позволяют осуществить полную переработку шлаков производства феррохрома в Казахстане. В настоящее время в Казахстане имеется избыток производства серной кислоты, поэтому становится целесообразным использование серной кислоты в качестве реагента для выщелачивания хрома из шлаков производства феррохрома. Можно ожидать, что в серной кислоте при определенных условиях, таких как нагрев, будет достигнута достаточно высокая степень извлечения хрома (III) в шлаках производства высокоуглеродистого хрома и в рафинированных феррохимических шлаках.

Ключевые слова: производство феррохрома, хромсодержащие шлаки, выщелачивание, разделение шлаков, серная кислота, шестивалентный хром, трехвалентный хром

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ҚЫШҚЫЛДЫҚ ӘДІСПЕН ФЕРРОХРОМ ӨНДІРІСІНІҢ ШЛАКТАРЫНАН ХРОМДЫ БӨЛІП АЛУДЫ АЙҚЫНДАУ

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Түйіндеме. Кіріспе: Қазақстан Республикасында өнеркәсіп қалдықтары көлемінің, оның ішінде феррохром өндірісінің айтарлықтай өсү үрдісі байқалады. Қазіргі уақытта табиғи ортаның техногенлік ластану проблемалары жыл сайын шиеленісіп, жаһанлық сипат ала басталы. Техногенді феррохром өндірісінің қалдықтарында суды, топырақты уландыратын, барлық тірі организмдердің белсенділігіне теріс әсер ететін өте улы және канцерогенді хром бар. Шлактардың курамында өнеркәсіптін әртурді салаларында колданылатын кунды компоненттердің айтарлықтай саны, ен аллымен, сактау кезінде кайтарымсыз жоғалатын хром бар. Биосфераға антропогендік кысымды төмендететін және табиғи ресурстарды тұрақты пайдалануды қамтамасыз ететін өнеркәсіптік қалдықтарды басқару процестерін дамыту басты міндет болып қала береді. Жұмыстын максаты: феррохром өндірісінің шлактарын өндеу әдісін тандауды негіздеу. Корытынды: Тазартылған және жоғары көміртекті феррохром өндірісінің хромы бар шлактарды кышкылмен өңдеу және кәдеге жарату бойынша заманауи ғылыми және патенттік әдебиеттерге талдау жүргізілді. Айта кету керек, феррохром өндірісінің шлактарын өндеудің әртүрлі әдістерінің сипатталған әдістері олардың қолжетімділігіне қарамастан, көп сатылы сипатқа ие және Казақстанда феррохром өндірісінің шлактарын толық өңдеуге мүмкіндік бермейді. Қазіргі уақытта Казақстанда күкірт қышқылын өндірудің артығы байқалады, сондықтан феррохром өндірісінің шлактарынан хромды шаймалау үшін реагент ретінде күкірт қышқылын қолданған жөн. Күкірт кышқылында қыздыру сияқты белгілі бір жағдайларда жоғары көміртекті хром өндірісінің шлактарында және тазартылған феррохром шлактарда хромды (III) алудың жеткілікті жоғары дәрежесіне қол жеткізіледі деп күтүге болады.

Түйін сөздер: феррохром өндірісі, құрамында хром бар шлактар, шаймалау, шлактарды бөлу, күкірт қышқылы, алты валентті хром, үш валентті хром

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