WASTES OF THE FERROALLOY PRODUCTION ARE RAW MATERIALS FOR THE CHEMICAL BRANCH OF INDUSTRY

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ABSTRACT

The ferroalloy production occupies a leading position in the economy of the Republic of Kazakhstan; therefore, one of the urgent tasks is to solve the issue of improving the environment protection. This issue includes the following tasks:

- *Introduction of new effective processes of dust collecting;*
- *Matters of the cleaning of flue gas and slimes; matters of the cleaning of flue gas and slimes;*
- *Neutralization and waste recovery.*

Creation of efficient Process flow schemes of the recovery of dispersed materials containing a target element of the ferroalloy being melted is a cost-effective and environmentally reasonable measure for improving the production profitability.

On the basis of the research carried out a Process flow scheme of processing of dust of the manganese alloys production has been proposed. A technological scheme of chromite dusts processing that includes the oxidizing roasting and subsequent obtaining of sodium bichromate by the method known in chemical technology has been elaborated.

KEYWORDS: *Chromite dusts, the sodium bichromate, manganese dusts and slimes.*

The major share of waste at all ferroalloy enterprises is comprised of slag and various dusts of gas cleaning.

As the main causes of environmental problems in the area of the ferroalloy production enterprises activity we should note imperfect technologies, using of outdated melting equipment, applying of low-efficiency schemes for gas cleaning and lack of conditions for capturing gaseous products, insufficient use of the tried-and-true technological methods of metallurgical raw materials processing while using which all the wastes would be processed at the source of their production and a proportion of materials being sent to dumps would be reduced to a minimum.

When smelting high-carbon ferrochrome by a carbothermic method, fine particles of chrome ore and a carbonic reducing agent are carried away from the furnace bath together with the flue gas consisting mainly of CO and trapped in the bag filters. An amount of the collected dust containing 25-30 % of Cr_2O_3 is 3-5 % of the weight of the burden material having been loaded into the furnace. When returning the collected dust to a storehouse of the burden material in order to mix it with chrome ore and feed it into the furnace, a flue-dust blowout is repeated that results in an increase of the circulating load in the dust collecting system.

The increasing of the dust content of a furnace gas complicates operation of the bag filters and transportation of dust to a storehouse of burden materials increases a dust content of the air in the operating space. In addition, a burden material permeability in the bath becomes worse and a steady yield of the technologic gaseous product of melting from the zone of reducing reactions becomes more difficult. Due to these disadvantages the captured chromium containing dust is frequently not recovered.

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To produce sodium bichromate - the main product in the production of chromium salts, a low-grade chromite ore is used. Sodium monochromat is obtained from this ore by means of oxidizing roasting in the mixture of soda and calcium oxide in the form of dolomite or limestone. Sodium monochromat is recovered by the water leaching; its solution is subjected to etching with a sulphuric acid to transform monochromat to dichromate.

This traditional method is used for processing dust of the ferrochrome production at the Aksu plant (Kazakhstan). The X-ray analysis of the dust showed the presence of chromospinelide of FeO (Cr, Al)$_2$O$_3$ composition and chromium oxide Cr_2O_3 in it. The following components: Fe – 5.5 %, Mn – 1.8 %, Cr (total) – 20.7 %, Cr_2O_3 – 30.2 %, Al_2O_3 - 20 %, CaO - 5 %, MgO - 15 % and others have been determined by the chemical analysis.

Table 1 shows the results of experiments on optimization of parameters of the oxidizing roasting of a burden material.

The burden material is a well-stirred mixture of chromous dust and different consumptions of sodium carbonate depending on the weight of the feedstock. The fineness was 0.075 mm.

Based on the experimental data (table 1) processed by means of the probabilistic-deterministic analysis, an extended mathematical model in the form of an equation of partial dependences given in Figure1 has been obtained:

$$\beta_{cake} = 147.7103 \cdot t^{-0.2487} \cdot \tau^{-0.02609} \cdot 0.9928^{N} \cdot N^{0.254}$$

Thus, the best conditions for roasting of dust of the ferrochrome production are as follows: temperature of 960^{o}C, duration 1.5 hours, consumption of sodium carbonate – 30 %.

When processing the calcined burden material (a chromate cake) with water, chromates of sodium and calcium, sodium aluminate and soda are leached from it into a solution. Under the effect of water other solid components of the cake are transformed into new mineral phases remaining in the slime or interacting with the system components. Thus, hydro-silicates, calcium carbonates and hydroxides of magnesium and aluminum, hydroaluminates of calcium are formed due to a slow hydration and hydrolysis.

The principal Process flow scheme of the sodium bichromate production includes the following main stages:

1. The cleaning of yellow lye from aluminum.

This step is performed by means of evaporation of the obtained sodium chromate solution with the initial content of 20 g/l up to its concentration of 30 g/l at 70-80^{o}C, when the process of an intensive crystallization of aluminum hydroxide begins.

2. The filtered solution is subjected to further concentration of yellow lye by means of evaporating the solution up to the concentration of 200 g/l.

3. The process of turning chromates into bichromates is called "etching" and in practice it is performed by dint of sulfuric acid according to the reaction:

$$2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

4. Concentration of red liquor (sodium bichromate) and its crystallization.

Thus, a technological scheme of chromite dusts processing that includes the oxidizing roasting and subsequent obtaining of sodium bichromate by the method known in chemical technology has been elaborated (figure 2).

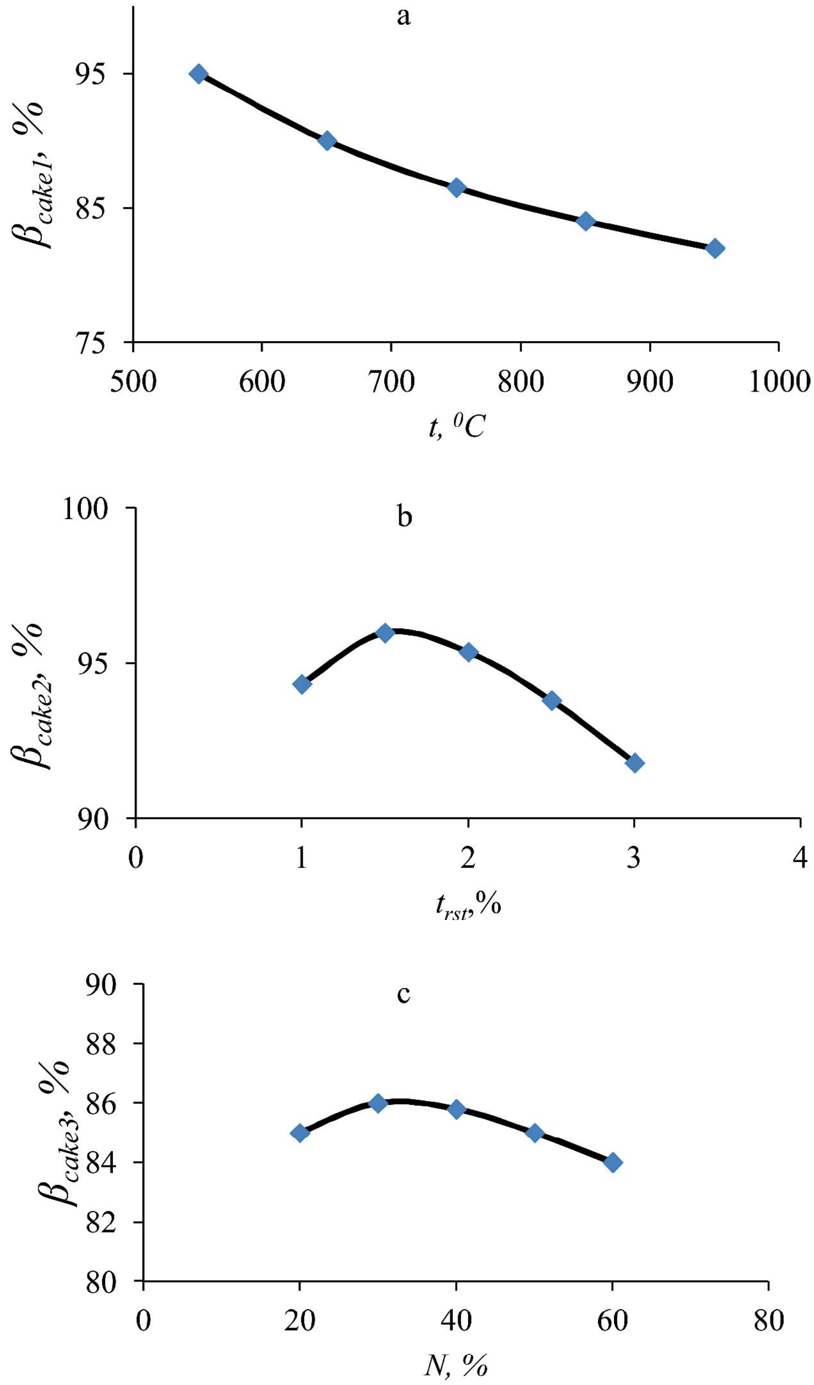
Table 1: The conditions of oxidizing roasting of dust of the ferrochrome production

Temperature t_{rst}, °C	**Time ofoxidizing roasting τ_{rst}, h**	**N, %**	**Yield of cake Experimental $B_{cake\ ex}$, %**	**Yield of cake Theoretical B_{cake} %**
560	1	20	94.33	94.67
560	1.5	30	95.98	96.75
560	2	40	95.36	95.96
560	2.5	50	93.80	93.63
560	3	60	91.79	90.42
660	1	30	92.84	93.76
660	1.5	40	92.04	92.99
660	2	50	90.43	90.73
660	2.5	60	88.42	87.62
660	3	20	88.88	87.52
760	1	40	89.55	90.64
760	1.5	50	87.78	88.43
760	2	60	85.73	85.40
760	2.5	20	86.11	85.31
760	3	30	87.80	87.18
860	1	50	85.77	86.57
860	1.5	60	83.58	83.60
860	2	20	83.85	83.51
860	2.5	30	85.44	85.34
860	3	40	85.06	84.64
960	1	60	81.95	82.11
960	1.5	20	82.03	82.02
960	2	30	83.48	83.82
960	2.5	40	83.05	83.14
960	3	50	81.75	81.12
R			0.9846	
t_R			610.8173	

Notes: the results of experiments ($\beta_{cake,\ ex.}$) and calculations ($\beta_{cake,\ th.}$);
R - coefficient of correlation; t_R - its signification

The water leaching of the obtained cake for the purpose of turning sodium chromate into a solution was carried out at 60°C, l:s (liquid: solid) = 4:1; it lasted 2 hours and the recovery degree of chromium reached 94.1 %.

The fundamental loss of manganese in the ferroalloy production is connected with transition of manganese oxides (over 30 %) into slag and 10 % of them - into a dust-and-gas phase; therefore, a search for rational Process flow schemes of recovery of manganese from slag, slimes and dust is important.



a – dependence on the temperature of roasting,
b – dependence on the time of roasting,
c – dependence on the consumption of Na_2CO_3 (N,%)

Figure 1: The partial dependences of the cake yield (β_{cake}, %)

Manganese dusts and slimes of the Aksu Ferroalloy Plant (Kazakhstan) are also a raw material for producing metallic manganese and its chemical compounds, in particular manganese dioxide. The fact that they are identical to oxidized manganese ores provided the basis for conducting the research on hydrochemical processing of these dusts.

The sulfuric acid leaching of manganese oxides is the core operation of the most schemes of hydrometallurgical processing of manganese-containing raw materials. Only manganese (II) is recovered into a sulfuric acid solution. Transition of psilomelane ($MnOMnO_2$) (a basic oxide compound in the form of which manganese is present in dusts of the silicomanganese production) into solution requires the presence of a reducing agent in sulfuric acid solution. A pyrite concentrate is used as such reducing agent.

By means of mathematical planning of the experiment using the probabilistic and deterministic method the influence of pyrite on the recovery of manganese dioxide when leaching with sulfuric acid has been studied. A pyrite concentrate (the Maykain deposit, Kazakhstan) having 96 % of the base material, 0.3-0.5 % of chalcopyrite, 0.5% of sphalerite and traces of galena, covellite and ferrous sulfate was used.

Determining factors of the leaching process are: temperature, duration of the process, an amount of pyrite being added, concentration of sulfuric acid. Based on the significant equations of a partial dependence a mathematical model of leaching of manganese dust with sulfuric acid in the presence of pyrite has been created in the form of a generalized equation:

$$Y_{calc.} = 3.7 * 10^{-6}(1.041x - 1.015)(4.2773x + 57.724)$$
$$(0.1369x^2 - 0.8993x + 61.028)(-0.0097x^2 + 1.2465x + 34.85)$$

On the basis of the equation the best conditions for leaching of manganese into a sulfuric solution have been selected: temperature of 70°C, duration of 3 hours, the concentration of sulfuric acid 5%, an additive of pyrite concentrate 90% of the weight of dust. A degree of manganese recovery was 95.8%.

It is most expedient to use ammonium sulphate in concentration of 150 g/l as a lixiviant both in this case and at electrochemical producing of metal manganese.

The manganese content in the solution when leaching the furnace-charge consisting of a pyrite concentrate and dust in the ratio of 1:1 by means of ammonium sulfate at temperature of 90°C, the ratio l : s = 4:1 was 22.4 g / l, that of iron was 0.06 g / l.

After removal of impurities we got a solution containing 30 g / l of manganese, 0.023 g / l of iron, 0.36 g / l of silicon; phosphorus and aluminum were not found. The concentration of ammonium sulfate in the solution was 160 g/l.

The optimal parameters of sulfuric acid leaching using the activated special coke as an intensifier have been determined: proportion of coal (fraction of 1 mm) to that of dust is 1:2, sulfuric acid concentration is 5 %, temperature is 80°C, l: s = 4:1. A degree of manganese recovery into the solution is 97.1 %, and that of iron is 0.7 %. A fraction of 1.0 mm obtained from long-flame bituminous coals of the Shubarkol deposit (Kazakhstan) according to the technology developed by Zh. Abishev Chemical-Metallurgical institute (Karaganda, Kazakhstan) has been used as a special coke. The activated special coke contains 92.3 % of carbon, 0.3 % of sulfur, and 0.97 % of iron.

Electrolysis of manganous sulphate solution (the solution concentration up to 90 g/l) was carried out in laboratory conditions in a two-chamber electrolyzer, the anodic and cathodic areas being separated by a cloth membrane (belting). The current density of 100-120 A/m^2 was maintained on titanium anodes, and that of 200-250 А/м^2 was maintained on steel cathodes. The current output was 95 %. The process temperature was 25-40 C, the electrolysis lasted 2 hours. By its chemical composition the obtained manganese dioxide met the requirements for the first quality in accordance with the GOST 25823-83. The content of mass fraction in the obtained electrolytic MnO_2 is 91.3 % that corresponds to the State standards.

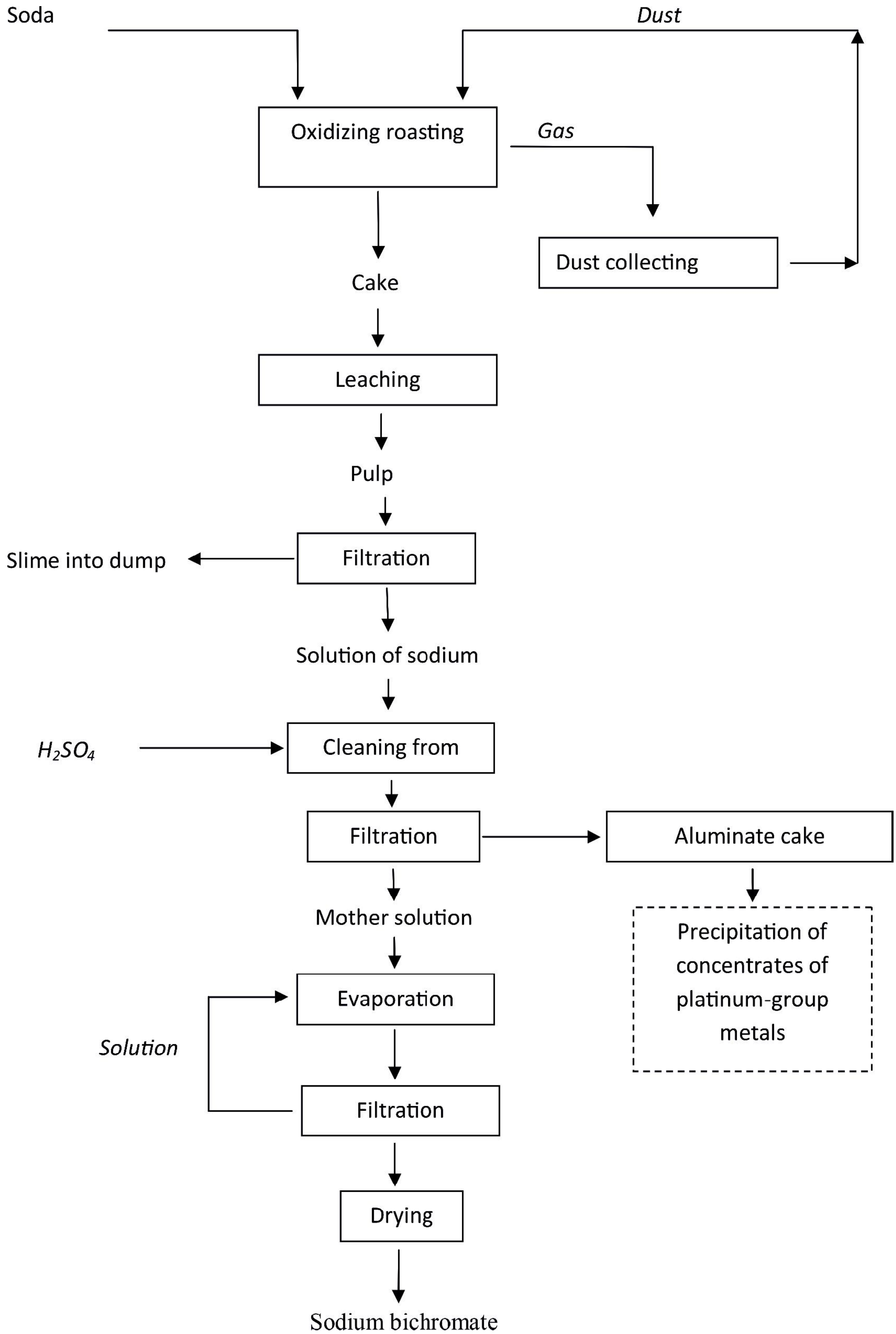


Figure 2: A technological scheme of obtaining sodium bichromate from dusts and slimes of the ferrochrome production

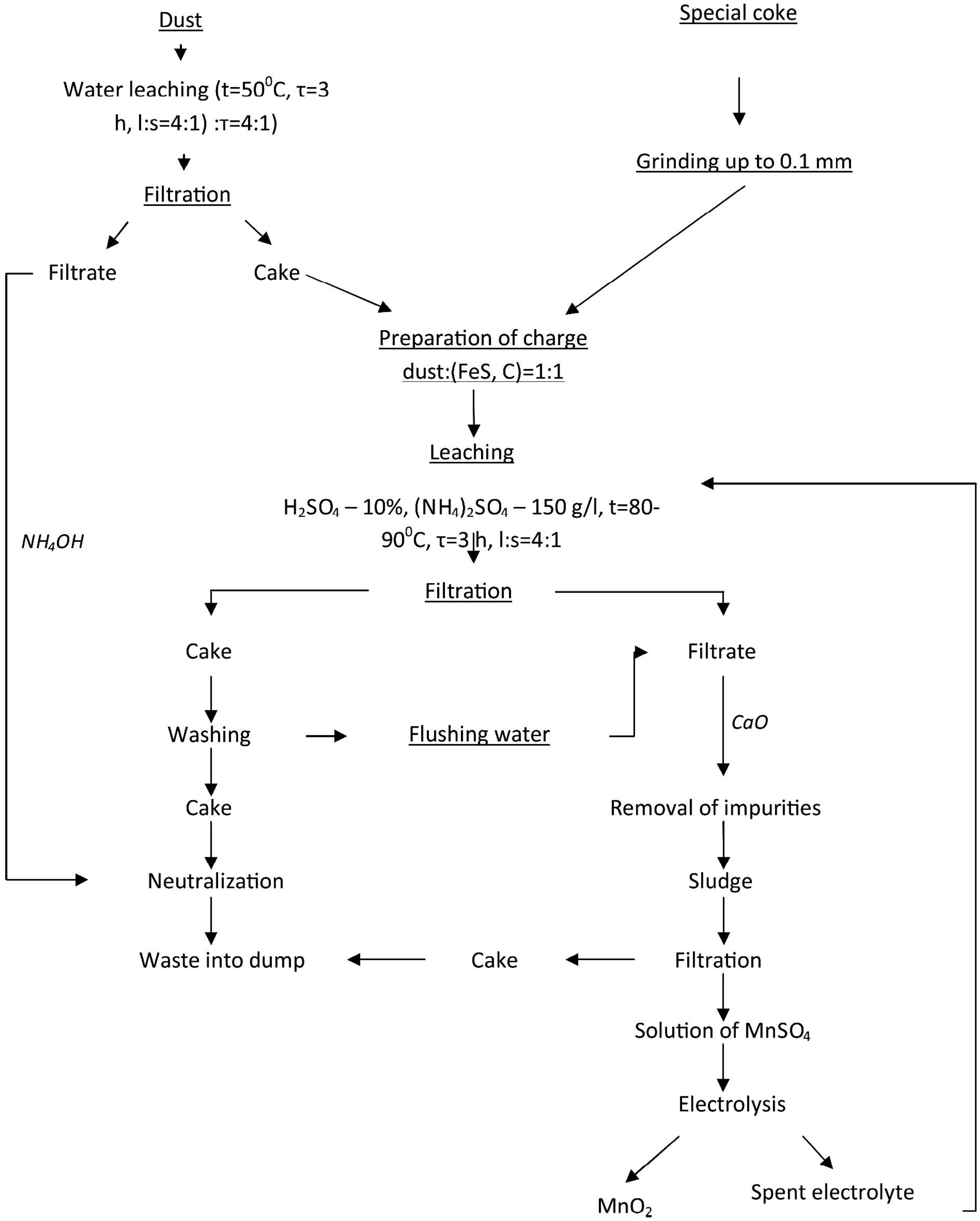


Figure 3: The Process flow scheme of processing of manganese dust of the ferroalloy production

Thus, on the basis of the research carried out a Process flow scheme of processing of dust of the manganese alloys production has been proposed (figure 3).