Extraction of Chromium from Carbon Ferrochromium Residual Wastes

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Abstract. This work reports the problem of processing residual wastes after producing carbon ferrochrome by recycling dust using a hydrometallurgical method with the purpose of extracting the basic component - chromium. The X-ray diffraction analysis results, chemical and granulometric compositions of dust from the carbon ferrochrome production are given. The method for the production of chemical-enrichment concentrate (CEC) by processing ferrous dust is described, with obtaining a middling product - sodium mono-chromate with its further reduction to chromium hydroxide, followed by autoclave leaching, and resulting in the production of chemically enriched chrome concentrate. The plant used for autoclave leaching and filtering is schematically depicted. The smelting process of metallic chromium using the ladle aluminothermic method is described.

Introduction

Today, metallurgical enterprises pay much attention to both the rational use of both internal material returns and industrial waste recycling. In recent years, a top-priority has been given to the disposal of ferroalloy production wastes and their maximum return to production processes that can result, in its turn, in saving material and energy resources and reducing production costs [1, 2].

One of the technogenic waste types after the production of high-carbon ferrochrome is dust (ferrous dust). This ferrous dust is formed in the production process of ferroalloys and is collected by a gas cleaning system fitted in the ore smelting furnace. When ferrochrome is melted in the open furnace, the volume of dust entrained makes 50 - 60 g/m^3, in some cases up to 100 g/m^3. The specific dust yield per 1 ton of ferrochrome for an open furnace is 25 - 75 kg/t [3]. The dust after the ferrochrome smelting has the following chemical composition in %: Cr_2O_3 22.5 – 43,6; SiO_2 10.0 – 15.5; CaO 0.2 – 0.4%; MgO 25.2 – 33.1; Al_2O_3 3.2 – 5.4; FeO 4.1 – 6.0; C 5.4 – 6.2; S 1.0 – 1.2.

A granulometric composition of dust depends on many factors and can vary greatly. The distribution of dust particles per fractions is given in Table 1.

Table 1. Distribution of dust particles per fractions.

Particle size, micron	>200	200 – 100	100 – 60	60 – 20	20 – 10	10 – 1	<1
Content, wt. %	34.5	12.3	19.0	25.0	7.5	1.65	0.05

Given the considerable amount of ferrous dust and high content of chromium oxide in it, recycling is an important task in modern technological scheme of ferrochrome production.

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According to the X-ray diffraction phase analysis, chromium in ferrous dust is present in the form of a complex compound (Mg, Fe) $CrAl_2O_4$, and this requires the application of a hydrometallurgical process to extract the main component, including the treatment of material with acids or alkalis solutions and transfer of the extracted component into a solution with its further extraction.

The process for obtaining chemical enrichment chromium concentrate consists of two stages:

1) Ferrous dust is processed to convert chromium from the complex compound into sodium monochromate and to receive a concentrated solution;

2) Sodium mono- chromate is reduced to chromium hydroxide, with further production of CEC.

The technology used in producing sodium mono- chromate is based on chrome ore enrichment and involves the oxidation heat treatment of a charge consisting of ferrous dust and soda ash (Na_2CO_3 not less than 98%) [4].

The component ratio is calculated based on the stoichiometric reaction:

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 = 4Na_2CrO_4 + 4CO_2 \quad (1)$$

The charge components thoroughly mixed in a drum mixer were subjected to the oxidation heat treatment at 1150 - 1250 °C for three hours in a muffle furnace. After cooling, the resulting sinter was ground to a fraction of less than 50 microns and X-Ray analyzed. The results of the X-ray diffraction phase analysis given in Figure 1 indicate that sodium mono- chromate was formed due to chromium contained in the dust. In addition, during the oxidative sintering the interaction of ferrous dust impurities (SiO_2, Al_2O_3, Fe_2O_3) with sodium results in forming silicates, sodium aluminates and ferrites.

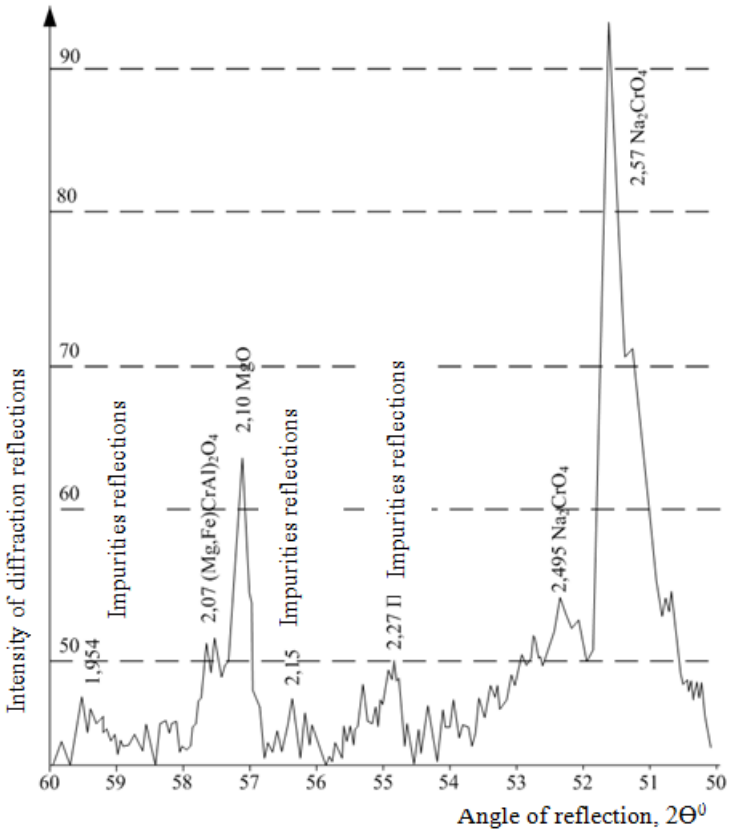


Figure 1. The X-ray diffraction pattern of a sinter

To extract the sodium mono-chromate from the sinter, the leaching process in water with a solid - liquid volumetric ratio of 1:1 was used [4]. The leaching was conducted in an autoclave at 70 - 90°C for one hour. In this process, the pulp consisting of the sodium mono- chromate solution and sludge was formed. Further separating the pulp in a Nutsche filter resulted in the formation of the sodium mono- chromate solution with a chromium concentration of 130 - 150 g /l and sludge with the following chemical composition, %: 0.9 – 1.2 Cr_2O_3; 7.4 – 8.5 FeO; 68.3 – 69.4 MgO 15.9 – 16.4 Al_2O_3. The content of impurities in the sodium mono- chromate solution does not exceed 30 mg/l.

During the second stage in producing CEC, sodium mono- chromate was reduced to chromium hydroxide. The process is based on the autoclave leaching of the solution at a temperature of 140 - 150 ° C and a pressure of 4 - 6 kg/cm^2 for one hour, with adding elemental sulfur according to the reaction in [6]:

$$4Na_2CrO_4+6S+(2n+1)\cdot H_2O \rightarrow 2Cr_2O_3\cdot nH_2O\downarrow+3Na_2S_2O_3+2NaOH. \quad (2)$$

Figure 2 displays the schematic equipment used.

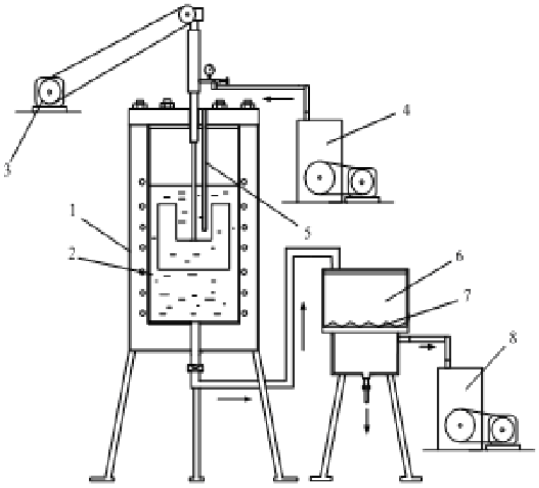


Figure 2. An autoclave with the mechanical mixing and Nutsch filter: 1 - reactor with paddle mixer (a rotation speed of 15 - 20 rev/min); 2 - sodium mono- chromate solution Na2CrO4; 3 – electric driver; 4 - compressor; 5 - thermocouple; 6 - Nutsch (suction) filter; 7 - filtering cotton cloth; 8 - vacuum pump

After an hour, the contents were pumped to the Nutsche filter and washed with running water; on the surface of the filtering cloth there appeared a bluish green precipitate (chromium hydroxide), the result of further heating at a temperature of 600°C was a gray-green powder with the following chemical composition, %: Cr_2O_3 95,8; FeO 3,9 [7-10]. The results of the X-ray diffraction pattern in analyzing CEC are shown in Figure 3.

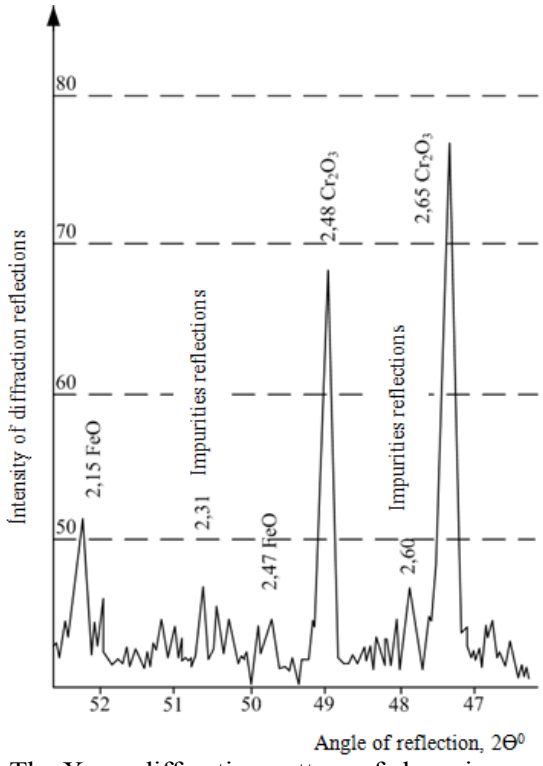


Figure 3. The X-ray diffraction pattern of chromic concentrate

The hydrometallurgical processing of the dust removed in the production of carbon ferrochrome enables us to obtain chemically enriched chromic concentrate, which can be used for the production of metallic chromium. The technological chart for the production of chromic concentrate using ferrous dust is shown in Figure 4.

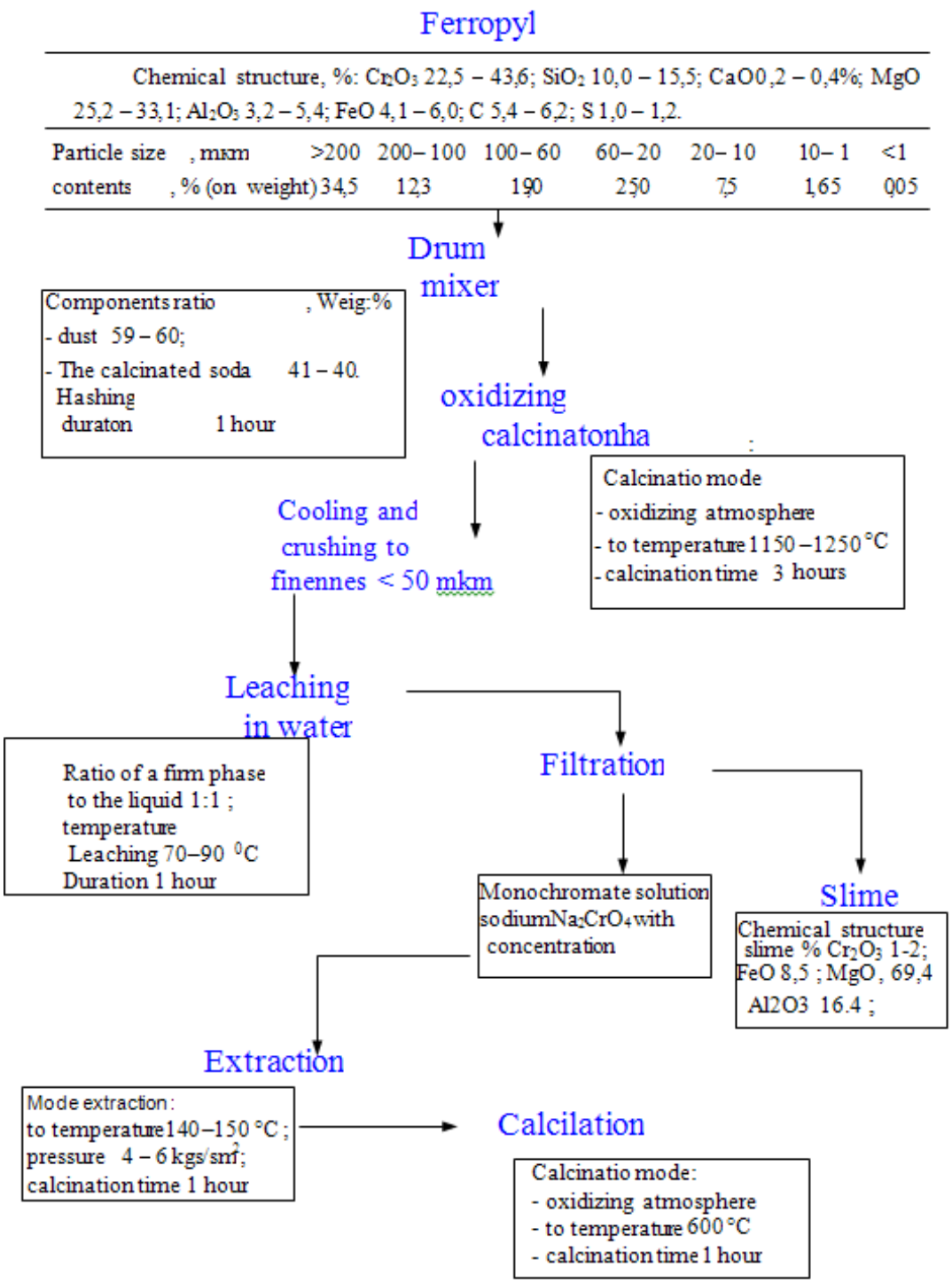


Figure 4. Block flow chart for extracting the chemical-enrichment chromium concentrate from ferrous dust

Metallic chromium was smelted using the out-of-furnace aluminothermic reaction. Charge materi-

als used were chromic CEC (Cr_2O_3 95.8%; FeO 3.9%), primary aluminum powder, sodium nitrate (> 99.0% $NaNO_3$) and fluorspar. The fraction of the charge materials was less than 1 mm. Magnesium swarf and potassium nitrate in a proportion of 4:1 were used as an ignition mixture. Smelting was conducted using the plant shown in Figure 5. It consists of a graphite crucible 1, where a weighted charge undergoes deep melting; a device to ignite the charge by heating a nichrome coil 2 connecting two electrodes 3; a pallet 4, on which the crucible with the weight and a mechanism for moving the electrodes with the spiral are placed. The electrodes are fixed to the roof, covering the crucible during the operation.

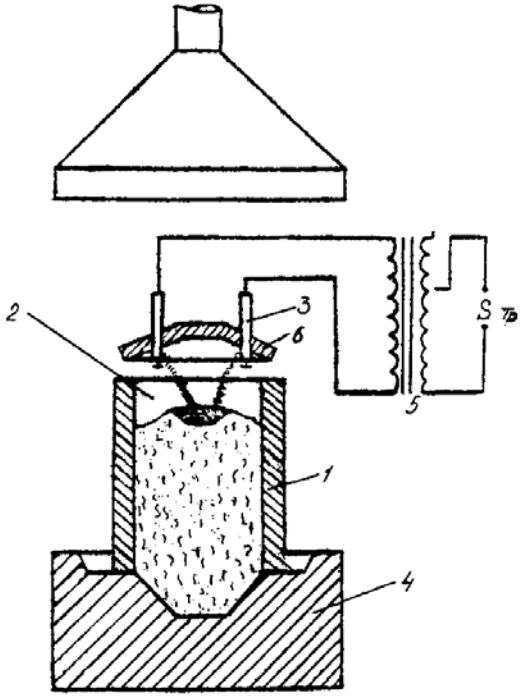


Figure 5. Schematic melting furnace: 1 - crucible; 2 - spiral; 3 - electrode; 4 - pallet; 5 - transformer; 6 - roof

Using a wheel, the device to ignite the charge was raised to its highest position; the crucible was then placed on the pallet and filled with the charge.

The ignition device was powered by transformer 5. Magnesium swarf and potassium nitrate in a proportion of 4:1 were used as an ignition mixture. A hollow was made in the center of the charge, and the hollow was then filled with the ignition mixture. After preparing the plant for work, current was supplied to bring the spiral to red heat, and the roof was lowered using the wheel till contact of the spiral with the ignition mixture. Magnesium inflamed and ignited the charge. After igniting the charge, current was turned off, then the process run spontaneously due to the heat of exothermic reactions.

The basic aluminothermic reactions used in producing ferrochromium are shown in Table 2.

Table. 2 - Basic aluminothermic reactions in ferrochrome production

Reaction	Oxygen content in oxide, %	Metal content in oxide, %	Aluminum content per 1kg oxide, kg	Thermal effect of reaction at 2227 °C, kJ	Thermal effect per 1 kg oxide, kJ	Specific heat of reaction at 2227 °C, kJ/kg
$Cr_2O_3 + 2Al + 2Cr + Al_2O_3$	31.6	68.4	0.36	- 394000	2590	1913
$3FeO + 2Al + 3Fe + Al_2O_3$	22/2	77.8	0.25	- 848250	3920	3140
$6NaNO_3 + 10Al = 3Na_2O + 3N_2 + 5Al_2O_3$	56.5	Nitrogen content 16.5	0.53	- 6871400	13470	8820

The process is spontaneous because of the heat generated due to the exothermic reactions for a period of 20 - 25 minutes.

The resulting metal and slag were analyzed using the X-ray diffraction; the results are given in Figure 6. The slag multiplicity is 2.4.

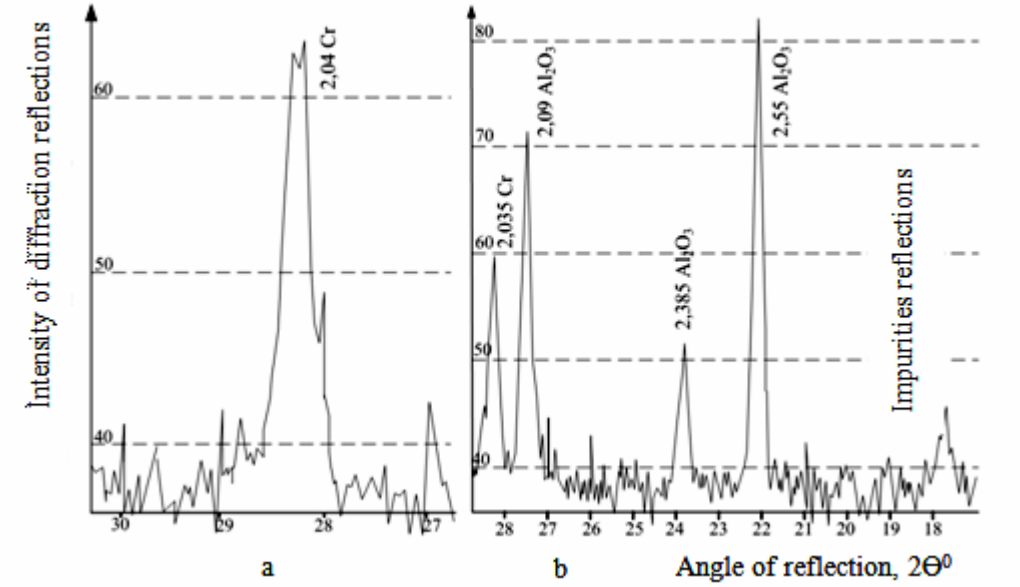


Figure 6. The X-ray diffraction pattern of metallic chromium (a) and slag (b)

The results of the X-ray diffraction analysis show that the metallic fraction of the reduced products is presented in the form of chromium. Chemical composition, %: 98.0 – 98.5 Cr, 0.4 – 0.5 Si, 0.5 – 0.7 Al, 0.6 – 0.8 Fe, 0.03 – 0.04 C, 0.02 – 0.03 S, 0.02 – 0.03 P. The alloy corresponds to GOST-5905-2004.

Conclusion

The X-ray diffraction analysis of slag has revealed that the slag contains metallic chromium. This is due to the fact that the main component of the slag is high-melting aluminum oxide that causes the metallic shot to tangle in the slag. In this connection, it is required to reduce a temperature for melting the slag and increase its flowability in liquid state.

On grounds of the results obtained in the experiments, it follows that chromium concentrate produced by recycling the dust from the ferrochrome production can be used for the production of standard metallic chromium.

Thus, the technologies developed for the purpose of rational utilizing dispersed materials, containing a target element in the smelted ferroalloy, are cost-effective and environmentally sound.

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