Thermochemical dephosphorization of brown iron ore concentrate at Kirovskoe deposit

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This paper presents the results of research on the dephosphorization of high-phosphorus brown iron ore concentrate obtained from the ore at the Kirovskoe deposit (Republic of Kazakhstan). The initial ore of this deposit is similar in its geological, structural, and chemical composition to the ore of the Lisakovskoe deposit, where beneficiation scheme consists of the following sequential technological operations: grinding, desliming, dry magnetic separation, reducing roasting and wet magnetic separation. The obtained concentrate, despite its high iron content, is non-compliant in terms of phosphorus content and requires additional processing to reduce the phosphorus content to the level which is acceptable for the metallurgical industry. According to the scheme, which includes such operations as grinding, desliming, dry and wet magnetic separation, and reducing roasting with addition of 3 % calcinated soda and 4 % coke to the charge, a concentrate with Fe content 63.9 % and P content 0.945 %, with a product output 86 %, was obtained from ore at the Kirovskoe deposit. The high-phosphorus concentrate obtained at the Kirovskoe deposit was leached by 5 % sulfuric acid solution, with a liquid/solid ratio 3:1 during 60 min, resulting in a dephosphorized concentrate with an iron content 65.3 %, phosphorus content 0.189 % and output 88.5 %. X-ray analysis showed that introduction of calcinated soda into the charge during roasting improves reduction of goethite and promotes formation of a nepheline-like phase, enriched with sodium and having high fluidity and low melting temperature. This phase facilitates penetration of oolites into cracks and effective removal of impurities, including phosphorus, during leaching.

Key words: high-phosphorus brown iron ore, combined beneficiation methods, oolites, desliming, magnetic separation, reducing roasting, calcined soda, dephosphorization, leaching, nepheline, electron probe microanalysis, Rietveld method
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Introduction

Brown iron ores are widely distributed in Kazakhstan. They form such deposits with large reserves as Lisakovskoe, Ayatskoe, Priaralskoe etc. Unique mineralogical and chemical composition of these deposits is quite different in comparison with other sedimentary iron ores, most often with increased phosphorus content (with forming iron-phosphate minerals) or in the form of adsorbed PO_4 ion, iron oxides and ferriferous silicates [1–3]. It is the cause of using combined beneficiation methods, including magnetic, roasting-magnetic and hydrometallurgical methods [4–8], during processing of such ores.

Based on the analysis of scientific data from technical literature on current state of processing of complex high-phosphorus brown iron oolite ores and concentrates, the combined thermochemical technological route [9, 10] is considered as the most prospective direction for manufacture of standard raw materials for conventional metallurgical stage. This technological route includes low-temperature roasting with consequent cinder leaching in order to transfer essential part of phosphorus in solution with concentration of the main iron mass in a non-soluble reminder. The optimal conditions of thermochemical processing of brown iron oolite concentrates at Lisakovskoe deposit were established experimentally [11, 12]; the maximal dephosphorization degree is achieved in these conditions [13–17].

High-phosphorus oolite brown iron ore from Kirovskoe deposit is characterized by the following chemical composition (%): general iron 37.95; silicon oxide 29.14; aluminium oxide 3.30; phosphorus 0.56; other 3.0+0.0 with hydrate moisture content up to 8.9 %. This ore is similar to ore from Lisakovskoe deposit in its forming conditions, structure and substantial composition.

Substantial ore composition, which was examined via the method of X-ray phase analysis, is presented mainly by hydrogoethite together with hematite; non-ore part contains mainly silicon oxide (quartzite) as well as alumosilicates and clay minerals [18, 19].

The scheme of ore beneficiation, which was developed in laboratorial conditions, consists of the following consequent technological operations: grinding, desliming, dry magnetic separation (DMS), reducing roasting, wet magnetic separation (WMS) [20]. Final magnetic concentrate with output 86 % is not standard for phosphorus content (0.945 %) despite high iron content (63.9 %). It requires additional processing of this concentrate via acid leaching, in order to obtain concentrate with acceptable phosphorus content for metallurgical industry. Manufacture of such concentrate is the aim of this research.

Methods and objects of research

Standard methods of chemical and diffraction X-ray analysis using PANalytical Empyrean sensor were applied for determination of phase-chemical composition of products after roasting, magnetic beneficiation and dephosphorization. Phases identification was carried out using PANalytical Highscore Plus © (V4.5) software, which is integrated with the data base of the International Center of Diffraction Data (ICDD) PDF 4+2018. Quantitative X-ray phase analysis (QPA) was conducted via the Rietveld method using TOPAS V6 software [21, 22].

When studying phosphorus distribution in the samples, electron probe microanalysis at 12 kV, 75 nA was used with holding during 30 ms. Mapping of the results was conducted for the randomly chosen areas of the samples, each of them covered the area with size 1024 × 1024 µm; they were reflected in a map with 1 µm step. The elements (Fe, P and other) were mapped using dispersion spectrometer by wave length (WDS), together with hyper-spectral X-ray data, which were collected with use of an energy dispersion spectrometer (EDS). After mapping, the data on distribution of the elements was processed using CHIMAGE software package.

High-phosphorus brown iron ore and dephosphorized concentrate, obtained from ore of Kirovskoe deposit, were the objects of this research.

Experimental part

To obtain concentrates, ore of Kirovskoe deposit was preliminary subjected to grinding (100 %) to coarseness class –2.0 + 0.0 mm and then to desliming with liquid/solid relation 4:1. Fe and P content in product after desliming was 38.4 % and 0.572 % respectively, with product output 83.2 %.

Dry magnetic separation (DMS) of product after desliming was conducted in the field with high intensity (1.1 T), with obtaining of low-magnetic intermediate product with output 74.15 % and Fe and P content 48.11 % and 0.712 % respectively.

In order to transfer feebly magnetic ore minerals (Fe hydroxide and hematite) in strong magnetic forms of iron oxides and to remove hydrate moisture, the material was subjected to roasting in reducing medium, at the temperature 850 °C during 60 min, with introduction of calcinated soda (3 %) and reducing agent (4 %) of coke, obtained from coal of Shubarkolskoe deposit, in charge. A product of heat treatment – magnetized cinder with fe content 55.4 % and P content 0.848 % was ground via dry method to coarseness ~80 % with class 0.071 + 0.0 mm and then was subjected to wet magnetic separation at the field intensity 0.08 T. Output of magnetic concentrate with the following content (%): Fe – 63.9; P – 0.945; Al_2O_3 – 5.12; SiO_2 – 3.41, was equal to 86 %.

High-phosphorus concentrate, which was obtained via such way, was directed to leaching by 5 % solution of sulfuric acid, with a liquid/solid ratio 3:1 during 60 min at the room temperature. The results of magnetic concentrate dephosphorization are presented in the **Table 1**.

X-ray patterns with magnetic fraction of ore, concentrate and dephosphorized concentrate after dry magnetic separation are presented in the **Fig. 1–3**. Interpretation of these X-ray patterns via the Rietveld method allowed to establish quantitative correlations for the following components: quartzite (SiO_2); goethite (FeOOH); siderite ($FeCO_3$); rutile (TiO_2); calcite ($CaCO_3$); spinel (Fe_3O_4); hematite (Fe_2O_3); fayalite (Fe_2SiO_4); wustite (FeO); maghemite (γ–Fe_2O_3); nepheline – nominal composition (Al3,84K0,57Na3,24Si4,16O16); and pseudobrookite ($FeTi_2O_5$).

The results of X-ray pattern examination of phases identification and their quantitative parameters for these products are shown in the **Table 2**. They present relative mass percents, composition of amorphous nepheline-like substance is identified on the base of external standard.

According to the data in the Table 2, DMS magnetic fraction (sample 1) includes Fe-rich minerals goethite (82 %) and siderite (11 %), while gang mineral composition consists of quartzite (6.8 %) and small amount of calcite (< 1 %).

Magnetite (79.4 %) is the main component in the concentrate (sample 2), it appeared as a result of transformation of the most part of goethite in magnetite and it is marked as "spinel". Additionally, 4.9 % of wustite, 1.4 % of fayalite and 0.5 % of hematite were revealed in the sample. Forming of 4.3 % of nepheline-like phase ($Na_3KA_{l4}Si_4O_{16}$), which is a

Table 1. Results of leaching of phosphorus concentrate, obtained from ore of Kirovskoe deposit

Product	Output, %	Content				Extraction			
		Fe	P	Al_2O_3	SiO_2	Fe	P	Al_2O_3	SiO_2
Concentrate	100.0	63.90	0.945	5.12	3.41	100.00	100.00	100.00	100.00
Dephosphorized concentrate	88.50	65.30	0.189	2.49	3.11	90.44	17.70	43.04	80.71

Table 2. The results of quantitative X-ray pattern examination

Sample	Concengtration of crystalline phase (relative ww %)								
	Quartzite	Goethite	Siderite	Spinel (magnetite)	Fayalite	Hematite	Wustite	Nepheline	Maghemite
Magnetic fraction of DMS ore (sample 1)	6.8	82.0	11.0	—	—	—	—	—	—
Concentrate (sample 2)	1.2	—	—	79.4	1.4	0.5	4.9	4.3	8.2
Dephosphorized concentrate (sample 3)	1.1	—	—	80.2	0.9	0.6	4.3	—	12.9

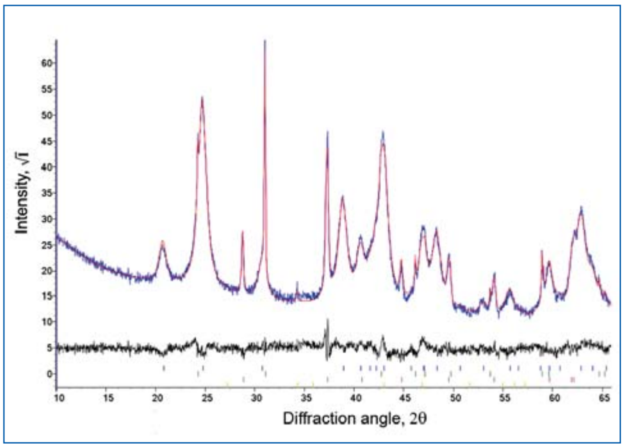

Fig. 1. The result of the Rietveld analysis, sample 1 (DMS magnetic fraction). Vertical lines are markers of Bragg peak for goethite, quartzite, siderite (downhill)

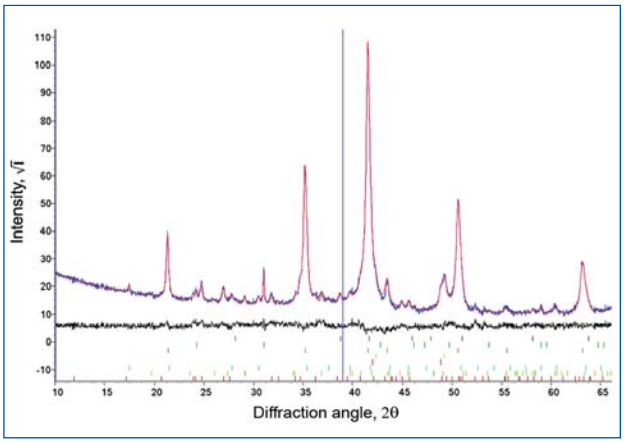

Fig. 3. The result of the Rietveld analysis, sample 3 (dephosphorized concentrate). Vertical lines are markers of Bragg peak for hematite, quartzite, spinel, wustite (1), wustite (2), maghemite and fayalite (downhill)

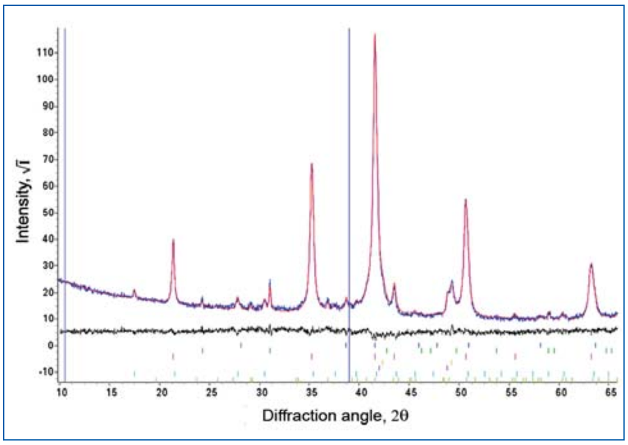

Fig. 2. The result of the Rietveld analysis, sample 2 (concentrate). Vertical lines are markers of Bragg peak for hematite, quartzite, spinel, wustite (1), wustite (2), maghemite, fayalite and hepheline (downhill)

sodium-rich alumosilicate – a product of reaction between calcinated soda and silicon oxides, aluminium in oolites and gang mineral, is considered as the most substantial variation in the phase composition of the sample 2. These effects were revealed previously by researchers during dephosphorization of Chinese oolite ore with high phosphorus content [23].

It was established that introduction of calcinated soda in the process of reducing roasting plays an important role in achievement of high degree of hematite reduction, as well as in forming of sodium-rich nepheline-like phase with increased fluidity and low melting temperature. This phase is able to penetrate in cracks of thermally destructured oolites and to clean them from harmful impurities (such as phosphorus, silicon and aluminium).

The sample 3 is identical to the sample 2 in phase composition, it differs only by absence of amorphous nepheline-like phase. Phosphorus-containing substances were not identified in the sample, because their concentrations are lower than their detection threshold for the method of X-ray phase diffraction analysis.

The results of electron probe analysis of DMS ore magnetic fraction, concentrate and dephosphorized concentrate are presented in the **Table 3**.

The results of electron probe mapping of the samples 2 and 3 displayed goethite transformation in magnetite 65 %, 12 % and maghemite 18 %, 66 % respectively. Presence of calcinated soda caused slight excessive reduction of oolites, what led to forming of bivalent Fe oxide – wustite 6 %, 12 %, and fayalite 3.7 %, 2.5 % respectively, what was also confirmed by the data of X-ray pattern analysis. It was mentioned earlier, that sodium presence leads to forming of nepheline-like phase – silicate Na/Fe 1.6 %, 0.51 %. Content of phosphates in the samples 1 and 2 corresponds to 0.042 % and 0.02 %, and in the sample 3 (dephosphorized concentrate) phosphates were not revealed.

The results of visual mapping during electron probe microanalysis, which was conducted for the samples 1–3, are presented in the **Fig. 4**, where lowering of phosphorus content during leaching of high-phosphorus concentrate is observed; it is confirmed by the data of chemical analysis.

Conclusions

High-phosphorus oolite brown ore from Kirovskoe deposit, with the following chemical composition (%): general iron 37.95; silicon oxide 29.14; aluminium oxide 3.30; phosphorus 0.56; other 3.0+0.0 with hydrate moisture content up to 8.9 % is similar in its geological, structural, and chemical composition to the ore of the Lisakovskoe deposit.

According to the beneficiation scheme at Lisakovskoe deposit, which includes such operations as grinding, desliming, dry and wet magnetic separation, and reducing roasting with addition of 3 % calcinated soda and 4 % coke to the charge, a concentrate with Fe content 63.9 % and P content 0.945 %, with a product output 86 %, was obtained from ore at the Kirovskoe deposit.

The high-phosphorus concentrate obtained at the Kirovskoe deposit was leached by 5 % sulfuric acid solution,

Table 3. The data of phases distribution (% of standard square) via electron probe mapping

Phase	Magnetic fraction of DMS ore (sample 1)	Concentrate (sample 2)	Dephosphorized concentrate (sample 3)
Goethite	64.0	–	–
Siderite	25.0	–	–
Magnetite	–	65.0	12.0
Maghemite	–	18.0	66.0
Wustite	–	6.0	12.0
Fayalite	–	3.7	2.5
Quartzite	6.1	0.72	0.34
Hematite	–	4.1	6.3
Al silicates	0.37	0.45	0.05
Phosphates	0.042	0.02	–
Fe Na silicates	–	1.6	0.51
Silicates	–	0.01	0.34

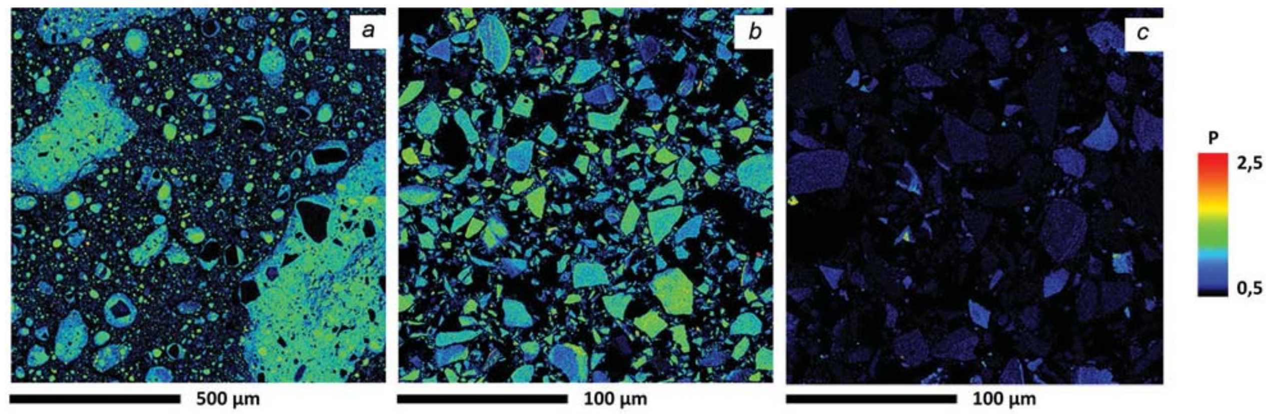

Fig. 4. Chart of phosphorus distribution, sample 1 (*a*), sample 2 (*b*), sample 3 (*c*)

with a liquid/solid ratio 3:1 during 60 min, resulting in a dephosphorized concentrate with an iron content 65.3 %, phosphorus content 0.189 % and output 88.5 %.

It was established that use of calcinated soda in the process of reducing roasting promotes essentially in reduction of hydrogoethite; forming of sodium-rich nepheline-like phase with increased fluidity and low melting temperature was revealed as well. This phase is able to penetrate in cracks of thermally destructured oolites and to clean them from harmful impurities (such as phosphorus, silicon and aluminium) during consequent acid leaching.

The results of visual mapping, which were obtained via electron probe microanalysis of the samples of magnetic ore fractions as well as phosphorus and dephosphorized concentrates, confirmed significant lowering of phosphorus content in concentrate after its leaching what corresponds to the received data of chemical analysis.

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