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Mechanism and kinetics of iron extraction from high silica boehmite-kaolinite bauxite by hydrochloric acid leaching

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Abstract: The chemical and mineral compositions of bauxite recovered from the Severoonezhsk Bauxite Mine (Arkhangelsk region, Russia) were studied by XRD, ICP-OES, TG/DSC, SEM, TEM, and Mössbauer spectroscopy. The iron-containing minerals of the bauxites were found to comprise alumogoethite (α -Fe_{1-x}Al_xOOH), alumohematite (α -(Fe_{1-x}Al_x)₂O₃), alumoakaganeite (β -Fe_{1-x}Al_xO(OH,Cl)), and chromite (FeCr₂O₄). The efficiency of Fe extraction from the bauxite by HCl leaching was 82.5% at 100 °C, HCl concentration of 10%, solid/liquid ratio of 1:10, and the process duration of 60 min, with aluminum loss from the bauxites below 4.5% of the total Al contents in the bauxite. Analysis of the kinetics of the iron leaching process proved diffusion to be the limiting stage of the process at 90–100 °C. Bauxite residue after leaching presented traces of α -Fe_{1-x}Al_xOOH and β -Fe_{1-x}Al_xO(OH,Cl), and most of the iron content was in the FeCr₂O₄. In bauxite residue after HCl leaching, in addition to iron oxide, the contents of chromium and calcium oxides significantly decreased. The iron chloride liquor after leaching contained the rare earth elements (REE) of 6.8 mg/L Sc, 4.1 mg/L Ce and 2.3 mg/L Ga.

Key words: bauxite; acid leaching; iron extraction; kinetics; Mössbauer spectroscopy

1 Introduction

The world-wide adopted standard method for alumina production is the Bayer process based on the alkaline leaching of bauxites [1]. The Bayer method can practically be applied to processing the bauxite feedstocks with alumina/silica ratios (μ_{Si} , Al₂O₃/SiO₂ mass ratio) above 7, the bauxites mined in tropical latitudes, such as in Guinea, Jamaica, Guyana [2]. The routes of freshly recovered bauxite delivery to alumina refineries in Europe can be time-taxing and costly. The logistics between the bauxite mines and the Russian alumina refineries may be stretching over 1.5×10^4 km [3]. The Russian aluminum manufacturers are on the outlook for the bauxite mines within the country's boundaries, as the way to lowering the minerals transportation expenditures [4]. Silica contents in Russian mined bauxites can be as high as 20-25 wt.%, which poses

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technological complications to their chemical treatments [5].

Currently, the bauxite deposits in the Northern Urals and Middle Timan are recovered by the technology combining sintering bauxites with sodium carbonate (Na_2CO_3) and limestone (CaCO₃) [6], followed by the alkali leaching. The acidic methods, alternative to the Bayer and sintering processes, enable leaching of all Al and Fe into the liquor, leaving behind the insoluble silica residues [7,8]. Iron is the major impurity of the acid-based technology, as it inhibits the processes of electrolysis or selective crystallization of aluminum chloride hexahydrate (AlCl₃·6H₂O). Therefore, efficient deironization of bauxites is a crucial technological step in the production of the sandy grade alumina [9–13].

The pyrometallurgical and hydrometallurgical methods are often used for the removal of Fe from the bauxite [14]. The pyrometallurgical methods are embodied by the carbothermic reduction of iron oxides hematite (α -Fe₂O₃) or goethite (α -FeOOH) into either magnetite (Fe₃O₄) or metallic Fe, followed by magnetic separation. At temperatures as low as 700-800 °C, the reduction of iron oxides may last up to 120 min [15-17], and at temperatures increased up to 1400-1450 °C the run time reduces down to 20 min [18,19]. The efficiency of Fe extraction via pyrometallurgical methods was not affected by the process temperature and reached 89%-92%, with FeO accounting for 1.0-2.5 wt.% in the non-magnetic fraction [20].

The hydrometallurgical methods rely on the leaching of bauxites with bacteria, alkali or acids. Bacterial leaching was proven to be the most effective for the processing of Fe^{2+} minerals, for example, chamosite ((Fe,Mg)₅Al(Si₃AlO₁₀)(OH)₈), where iron extraction exceeded 95% [21]. The extraction of Fe³⁺ from minerals like α -FeOOH and α -Fe₂O₃ did not exceed 45% [22]. Simultaneous leaching of 50% and 22% of alumina and silica respectively, was found to be a significant disadvantage to the bacterial method [23].

For Bayer method, the reductive digestion of high iron-bauxite at 260-270 °C for 60-90 min with adding of iron powder (10 wt.% with respect to bauxite mass) or glycerol (2 g/L C₃H₈O₃) leads to the formation of α -Fe₂O₃ or Fe₃O₄ from α -FeOOH. Further enrichment methods allow to obtain

separate iron concentrate (total Fe content more than 50 wt.%) [24]. This approach can decrease the red mud emission of about 70% compared with the current emission [25].

In comparison, acid leaching predominantly uses oxalic $(H_2C_2O_4)$, sulfuric (H_2SO_4) , and hydrochloric (HCl) acids. The H₂C₂O₄ leaching extracted 34%-85% iron into the liquor [26-28]. Iron oxalate (FeC₂O₄·2H₂O) can further be precipitated from the liquor after irradiation with ultraviolet light enabling the regeneration of $H_2C_2O_4$ [29]. The H_2SO_4 -assisted leaching of iron from bauxites or red mud is a two-step process and is preceded by the roasting stage at 550-600 °C in the 60 min duration, which allows the extraction from 47% to 98% of iron and 30% of potassium [30,31]. As a further modification, roasting of bauxites with ammonium sulfate $((NH_4)_2SO_4)$ can be carried out at a lower temperature of 450 °C, where further water leaching of the obtained sinter extracts up to 90% of aluminum into the solution, in addition to the iron [32]. However, the H₂SO₄-leaching of Fe₂O₃ from ash can be performed without the preliminary roasting, with extractions reaching up to 90% [33]. The HCl-leaching is the most effective technique sustaining the extractions of as much as 90% of iron into the liquor, regardless of the mineral composition of the feedstock ores [34-36]. In addition to iron, the HCl-leaching could as well target the extraction of calcium $(Ca(CO_3)_2)$ and magnesium carbonates $(Mg(CO_3)_2)$ [37]. The Al losses were shown to be non-exceeding 5%-6% in cases where HCl-leaching was applied to the bauxites that were composed of boehmite $(\gamma$ -AlOOH) and kaolinite $(Al_2(Si_2O_5)(OH)_4)$ as the main Al-containing mineral [38]. The high-pressure leaching techniques enabled more intensive dissolution of boehmite and kaolinite or other aluminosilicates by HCl, leading to Al extractions up to 90% [39,40]. Leaching in atmospheric conditions allowed separation of the major part (more than 80%) of iron from bauxites, followed by the extraction of iron chloride (FeCl₃) with aliphatic and aromatic diluents, its further concentration, and regeneration of HCl back into the ongoing process [41-43]. One exemplary regeneration of HCl involved spray drying of the FeCl₃ liquor at 430-470 °C, yielding gaseous HCl and Fe₂O₃ in the solid residue [44].

In this work, we aimed to emulate the cost-effective and facile hydrometallurgical method of Fe-extraction from the silica-rich Severoonezhsk bauxite. The current study emphasized the stage of hydrochloric deironization of the bauxite and sought to refine the technological parameters of the HCl-leaching process. Therefore, herein we dedicated our efforts towards the investigation of the kinetics and mechanism of HCl-leaching of the Fe-minerals from the boehmite–kaolinite bauxite, as well as optimized the HCl-leaching parameters, and evaluated the efficiency of the HCl-leaching stage of the process.

2 Experimental

2.1 Raw materials

The ground and classified (particle size less than 100 μ m) bauxite sample used in this research was collected from Severoonezhsk Bauxite Mine located in the Arkhangelsk region of Russia (N62.562530°, E39.690204°). Analytical grade hydrochloric acid (424 g/L) (Componet-Reaktiv LLC, Russia) was used in the leaching process. Distilled water was used to dilute the hydrochloric acid.

2.2 Iron removal from Severoonezhsk bauxite

Figure 1 shows the proposed flowsheet of the iron removal method applied to the Severoonezhsk bauxite, which included the following stages: bauxite leaching with HCl, iron concentration using solvent extraction, pyrohydrolysis of the obtained saturated solutions to produce iron oxide pigment. After the solvent extraction, the aluminum chloride solution is directed to the autoclave leaching of bauxite residue for further Al extraction. In the current study, we focused on the first stage of the proposed technological flowsheet: the hydrochloric acid leaching for Fe extraction.

Leaching of iron from bauxite by hydrochloric acid was conducted in the 500 mL flat bottom flask; the reaction agitated using the US-1500S magnetic stirrer (ULAB, Saint Petersburg, Russia). The bauxite load in the range from 30 to 100 g was admixed with 400 mL of HCl at the stirring rate in all tests maintained at 350 r/min. The HCl leaching was performed at temperatures of 80, 85, 90, 95, and 100 °C, while HCl concentrations were varied at 51, 77, 105, 132, and 161 g/L. The leaching lasted for 60 min, and the solid/liquid (S/L) ratios were 1:4, 1:6, 1:8, 1:10 and 1:12. Following the leaching, the mineral pulp was vacuum-filtered to separate the FeCl₃ solution from the solid residues, which were further rinsed with 1 L distilled water and air-dried at 105 °C for 240 min prior to the analysis.



Fig. 1 Flowsheet of iron removal process from Severoonezhsk bauxite

The efficiency of iron leaching (α) was calculated by

$$\alpha = [VC_{\rm Fe}/(mw_{\rm Fe})] \times 100\% \tag{1}$$

where C_{Fe} is the iron concentration in the filtrate detected by inductively coupled plasma optical emission spectrometry (ICP-OES), g/L; V is the volume of the iron chloride solution, L; m is the mass of the bauxite load used in each individual experiment, g; w_{Fe} is the content of the iron in the crude bauxite, %.

2.3 Bauxite roasting

For Mössbauer analysis, the samples of the raw bauxites and the bauxite residue after HCl leaching were roasted under air atmosphere in open corundum crucibles using muffle furnace HTC 03/18/3N/PE (Nabertherm, Lilienthal, Germany), heating time to the temperature 700 °C was 30 min, sample mass was 10 g, and the roasting time was 60 min.

2.4 Physical-chemical characterization of Severoonezhsk bauxite

2.4.1 Chemical composition

The chemical compositions of the raw bauxites and the bauxite residue after the HCl leaching, and the co-obtained FeCl₃ liquor were analyzed by ICP-OES using an atomic absorption spectrometer AA-240FS (Varian, Melbourne, Australia).

2.4.2 Crystal phase properties

The X-ray diffraction (XRD) analysis of the raw bauxites and the bauxite residue after the HCl leaching was performed using an Ultima IV diffractometer (Rigaku, Tokyo, Japan), the 2θ scattering angles were ranged from 9° to 100° at 0.02° increment, with the Cu K_a tube pre-set to 40 kW and 30 mA used as an X-ray radiation source. The experimental XRD data were qualitatively processed through the PDXL built-in software (Rigaku, Tokyo, Japan).

2.4.3 Mössbauer spectroscopy

The Mössbauer analysis results of raw bauxite, bauxite residue after leaching and samples after roasting at 700 °C were obtained using a spectrometer MS1104EM (Cordon, Rostov-on-Don, Russia) at (25±3), (-73±0.5) and (-195±0.5) °C in a vacuum cryostat. The ⁵⁷Co nuclei in a Rh matrix with 47 mCi activity in a Rh matrix (RITVERC, Saint Petersburg, Russia) were used as the γ -radiation source. The Mössbauer spectra were analyzed using SpectrRelax 2.4 software. The values of chemical shifts were presented relative to α -Fe.

2.4.4 Particulate bauxite morphology

The analysis of the surface morphology, microstructure, and elemental composition of the raw bauxites and the bauxite residue after the HCl-leaching was carried out via a combination of scanning electron microscopy (SEM) and transmission electron microscopy (TEM), using the JEM 2100 (JEOL, Tokyo, Japan) and Vega 3 (Tescan, Brno, Czech Republic) microscopes, respectively. Both microscopes were equipped with the energy dispersive X-ray (EDX) detectors (Oxford Instruments, Abingdon, United Kingdom). 2.4.5 Bauxite phase properties

The mass and temperature changes of the raw bauxite sample during the phase transitions were detected via differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), using the Q600 thermal analyzer (Netzsch, Selb, TA Instruments). The heating ramp was pre-set to be 10 °C/min within the temperature span of 100-1000 °C in the air atmosphere.

3 Results and discussion

3.1 Physical-chemical characterization

The chemical composition of Severoonezhsk bauxites was determined with the ICP-OES analysis, and the quantitative data are shown in Table 1. As is seen from Table 1, the μ_{Si} of the examined bauxite was 2.04, thus (as stated above) rendering as economically inefficient the use of the Bayer process for the alumina production from the Severoonezhsk bauxite. A relatively high 0.86 wt.% of Cr₂O₃ poses a significant technological obstacle for the further bauxite treatments by sintering process, as the final product has a high likelihood of Cr⁶⁺-contamination. Scandium level of 100 mg/kg makes possible for its full recovery through either solvent extraction or sorption on resin [45,46].

Table 1 Chemical composition of bauxites recoveredfrom Severoonezhsk deposit (Arkhangelsk region,Russia), as analyzed via ICP-OES (wt.%)

_												
	Al_2O_3	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO							
	49.26	24.18	5.56	2.94	0.88							
	Cr ₂ O ₃	LOI [*]	Sc**	Ga ^{**}	Ce ^{**}							
	0.86	16.02	100	60	120							
_												

* Loss on ignition at 1000 °C; ** in mg/kg

The mineral composition of raw Severoonezhsk bauxite was previously analyzed [47]. The iron content of the bauxite did not exceed 6 wt.% (Table 1) and was evenly distributed between goethite and hematite. The main Al-based minerals that comprised the bauxite were boehmite, kaolinite, gibbsite, and muscovite. Iron was contained mainly in inclusions of hematite and goethite, and titanium, in the form of anatase. The bauxites studied herein additionally comprised negligible inclusions of quartz and gypsum.

The analysis of the thermal and phase profiles of the Severoonezhsk bauxite was performed via paired TGA and DSC. As is seen from the thermogram in Fig. 2, removal of water from the bauxite sample proceeded in three stages. The initial loss of 1% of the bauxite mass took place during the heat-up within the 100–120 °C span, which was indicated by a short step on the TGA-curve, shadowed by a slight DSC-endotherm at 121 °C. At this stage, the dehydration could be attributed to the removal of the physically absorbed moisture and partial dehydration of the gypsum accompanied by the formation of calcium sulfate hemihydrate (CaSO₄·0.5H₂O) as outlined by Reaction (2) [48].



Fig. 2 TGA and DSC curves of Severoonezhsk bauxite recorded for initial sample of 33.902 mg, and air-heated at ramp of $10 \text{ }^{\circ}\text{C/min}$ from 28 to $1000 \text{ }^{\circ}\text{C}$

The so-formed $CaSO_4 \cdot 0.5H_2O$ was then converted to calcium sulfate anhydrite (CaSO₄) upon further heating at 200 °C, as depicted by Reaction (3) [49]. The second stage of bauxite dehydration accounted for more than 3% of mineral's mass loss and was indicated by a steep dip on the TGA curve at 250-300 °C, as corresponded to the pronounced endotherm at 278 °C on the DSC curve. The second stage dehydration was driven by the decomposition of aluminum and iron hydroxides according to Reactions (4) and (5). The final third stage of mass loss of bauxite by 10% could be observed during a further heat-up of the sample at 490-560 °C, where Al-containing boehmite, the kaolinite, and muscovite underwent dehydration. Boehmite and kaolinite were entirely decomposed as depicted in Reactions (6) and (7), respectively, with the formation γ -Al₂O₃ and meta-kaolinite of (Al₂Si₂O₇) [50]. At the same time, dehydration of muscovite was onset at 450 °C and gradually progressed until the testing temperature reached 950 °C [51], which could be related to the synthesis of orthoclase (KAlSi₃O₈) and sillimanite (Al₂SiO₅), as depicted by Reaction (8). The third stage dehydration could likewise be traced on the DSC curve by a steep endotherm peak at 520 °C, while the chemical conversion of muscovite could be evidenced by a small exothermic peak on the DSC curve at 980 °C [52].

 $CaSO_4 \cdot 2H_2O(s) \rightarrow CaSO_4 \cdot 0.5H_2O(s) + 1.5H_2O(g) (2)$

 $CaSO_4 \cdot 0.5H_2O(s) \rightarrow CaSO_4(s) + 0.5H_2O(g)$ (3)

$$2\mathrm{Al}(\mathrm{OH})_3(\mathrm{s}) \rightarrow \gamma - \mathrm{Al}_2\mathrm{O}_3(\mathrm{s}) + 3\mathrm{H}_2\mathrm{O}(\mathrm{g}) \tag{4}$$

$$2FeOOH(s) \rightarrow Fe_2O_3(s) + H_2O(g)$$
(5)

$$2AIOOH(s) \rightarrow \gamma - Al_2O_3(s) + H_2O(g)$$
(6)

$$Al_2Si_2O_5(OH)_4(s) \rightarrow Al_2Si_2O_7(s) + 2H_2O(g)$$
(7)

$$\begin{array}{ll} \text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2(s) + \text{SiO}_2(s) \rightarrow \\ \text{KAlSi}_3\text{O}_8(s) + \text{Al}_2\text{SiO}_5(s) + \text{H}_2\text{O}(g) \end{array} \tag{8}$$

3.2 Mössbauer spectroscopy

The XRD method lacks sensitivity, especially in the X-ray amorphous phase characterization of the mineral forms of iron in the Severoonezhsk bauxite. Therefore, the Mössbauer spectroscopy was used to characterize the iron phases in the raw and post-leached bauxite, as this method provides fine energy resolution and can detect subtle changes in the environment of the Fe atoms.

The Mössbauer spectra recorded for the crude bauxite included a number of sub-spectra in the forms of sextets and doublets, and the subspectra numerated and colored in correspondence to the related sub-group in Fig. 3 and Table 2. As is distinctly seen from Mössbauer absorption spectra of the raw bauxite obtained at 25, -73, and -195 °C, most sub-spectra exhibited temperature sensitivity of the spectrum intensity, width, and magnitude of magnetic splitting. The spectrum obtained at 25 °C (Fig. 3) showed an intense paramagnetic doublet as well as the low-intensity sextet with noticeably distorted lines in the central part of the spectrum. This sextet encased, at least one more additional "internal" sextet composed of broad resonance lines (Group II, Table 2). The overall pattern of the 25 °C-spectrum of the Severoonezhsk bauxite closely corresponded to that of bauxite recovered from the Trombetas Mines and measured elsewhere [53]; however, the relative areas of the paramagnetic and magnetically ordered portions in our spectrum were at least five times higher.



Fig. 3 Mössbauer absorption spectra of Severoonezhsk bauxite measured at 25, -73, and -195 °C

Sub-				25 °C				−73 °C				−195 °C					
spectrum No.	Group	Phase	δ	$\Delta(=2\varepsilon)/(\mathrm{mm\cdot s}^{-1})$	$\Gamma_{\rm exp}$	$H_{\rm eff}/(10^7{\rm A}{\cdot}{ m m}^{-1})$	<i>S</i> /%	δ	$\Delta (=2\varepsilon)/(mm \cdot s^{-1})$	$\Gamma_{\rm exp}$	$H_{\rm eff}/(10^7{\rm A}{\cdot}{\rm m}^{-1})$	<i>S</i> /%	δ	$\Delta(=2\varepsilon)/(\mathrm{mm\cdot s}^{-1})$	Γ_{exp}	$H_{\rm eff}/10^7{\rm A}{\cdot}{\rm m}^{-1}$) <i>S/</i> %
1#	Ŧ	(T. 11) O	0.37	-0.21	0.33	4.0696	16.4	0.43	-0.20	0.31	4.1576	20.6	0.48	-0.22	0.33	4.2128	29.91
2#	1	α -(Fe _{1-x} Al _x) ₂ O ₂	0.36	-0.19	0.57	3.9128	11.2	0.42	-0.21	0.39	4.0368	7.8					
3#			0.37	-0.29	0.57	2.9440	6.4	0.42	-0.23	0.30	3.6168	5.1	0.47	-0.24	0.43	3.9608	25.5
4#	II	α-Fe _{1-x} Al _x OOH	0.31	-0.38	0.71	2.5680	3.7	0.42	-0.27	0.48	3.4640	5.6	0.48	-0.28	0.39	3.8064	9.0
5#			0.42	-0.29	6.23	1.5280	32.3	0.42	-0.18	2.13	3.2320	31.7	0.45	-0.23	0.65	3.6160	10.3
6#													0.61	-0.47	1.14	3.2160	8.2
7#	III	β -Fe _{1-x} Al _x O-	0.30	1.06	0.63		7.8	0.55	0.03	1.29	1.8800	11.6	0.92	-0.47	0.97	2.1040	6.73
8#		(011,01)	0.36	0.51	0.35		20.5	0.41	0.64	0.53		10.95	0.47	0.74	0.59		6.37
9 [#]		Fe ²⁺ _{Oh}	0.63	1.48	0.25		1.09	0.55	2.00	0.60		5.86	0.62	2.57	0.28		1.94
10#	IV	$Fe_{Oh}^{2.5+}$	1.16	2.53	0.25		0.57	1.15	2.70	0.25		0.87	1.22	2.85	0.41		2.06

Table 2 Phase parameters of Severoonezhsk bauxites attributed to Mössbauer spectra measured at 25, -73, and -195 °C

 δ -Isomer shift; Δ (=2 ε)-Quadrupole splitting; Γ_{exp} - Line width; H_{eff} - Hyperfine magnetic field; S - Relative area of a subspectrum

On the contrary, RAJ et al [54] measured Mössbauer spectra of bauxites mined in Tamil Nadu where the intensity ratio of the paramagnetic to magnetically ordered portions was higher than that of the spectra in Fig. 3 in this work. As the Mössbauer spectra of the above reference study had no "internal sextet", we concluded that the Fe-phases of the Severoonezhsk bauxite were similar in chemical composition to the bauxites recovered in Trombetas and Tamil, with the relative content of the Fe-phases dependent on the geographical source deposit.

The spectral profiles dramatically changed with the temperature lowered down to -73 °C (Fig. 3): intensity of the doublet decreased by 75%, with the lines of the "external" sextet noticeably narrowed and intensified. The temperature drop altered the profile of the "internal" sextet: increased intensity and magnitude of the magnetic splitting could be observed, as well as the decreased width of the resonance lines. The bands of the "internal" sextet were not co-symmetric and were strongly broadened in the interior of the spectrum.

The spectral pattern of the total doublet, internal, and external sextets preserved at scanning temperature of -195 °C, but their lines noticeably narrowed and intensities magnified. The "external" sextet's magnetic splitting magnitude at -195 °C approached that of the "outer" sextet, but did not reach it, thus both sextets were well resolved in the spectrum. At the same time, the "outer" sextet contained the noticeably narrowed lines. Intensities of the paramagnetic doublet drastically decreased upon cooling to -195 °C, which partially impaired its resolution. Overall, the cryo-temperature spectrum of the Severoonezhsk bauxite of our study was patterned similarly to that published elsewhere [53], with the exception that the magnetically ordered part of our Mössbauer spectrum had a higher resolution. This in turn could be explained by the presence of a single Fe-phase in the Severoonezhsk bauxite corresponding to the "external" sextet, while the Trombetas bauxite could contain at least two phases.

We used the following model to analyze the contents of bauxite: all collected Mössbauer spectra were described as a superposition of ten subspectra, which could be divided into four groups, each corresponding to a distinguished Fe-containing phase (Table 2).

The "external" sextet described by subspectra $1^{\#}$ and $2^{\#}$ (Group I, Table 2) referred to alumohematite (α -(Fe_{1-x}Al_x)₂O₃), where the Al atoms isomorphically replace a part of Fe atoms [55]. Aluminum-substituted hematite is typically characterized by low magnitudes of the magnetic splitting (compared to α -Fe₂O₃) and the invariance of the sign of the quadrupole displacement with decreasing temperature (the absence of the Morin transition) [56].

Mössbauer spectra of goethite feature a strong temperature sensitivity towards the magnetic hyperfine splitting [57], and the "inner" sextet therein is described by Subspectra $3^{\#}-5^{\#}$ (Group II, Table 2). Spectra of bauxite showed the isomorphic substitution of Fe with Al atoms, i.e., the formation of alumogoethite (α -Fe_{1-x}Al_xOOH) [58], since the maximum value of magnetic splitting at -195 °C was limited to 3.9605×10^7 A/m (Table 2) and did not reach the typical for the pure goethite [59].

The paramagnetic portion of the Mössbauer spectra is typically referred as superparamagnetic fractions of hematite [60] and/or goethite [53]. As is seen from the obtained spectral data, the downshift of the scanning temperature from 25 to -195 °C did not practically alter the total relative area of the subspectra $1^{\#}$ and $2^{\#}$, $3^{\#}-5^{\#}$, and $6^{\#}-8^{\#}$ corresponding to Groups I, II, and III, respectively. Subspectra $6^{\#}$ and $7^{\#}$ could not be attributed to Group II, due to the preset of hyperfine Mössbauer parameters involved, i.e. isomeric and quadruple shifts significantly differing from that of Subspectra $3^{\#}-5^{\#}$ (Table 2). A noticeably increased isomeric shift of Subspectra $6^{\#}$ and $7^{\#}$ with decreasing temperature exceeding the expected temperature increment ΔT for the second-order Doppler shift could indicate the participation of Fe atoms in electron exchanges with the neighboring transition elements. It should thus be assumed that Subspectra $6^{\#}$ and $7^{\#}$ could characterize Fe atoms substituted with aluminum and/or transition metals in minerals other than alumohematite or alumogoethite, for example, in akaganeite (β -FeO(OH,Cl)) [61,62], or in the Al-containing mineral carrying Feadmixtures [63], or possibly in another superparamagnetic form.

Subspectra $9^{\#}$ and $10^{\#}$ (Group IV, Table 2) are new for bauxite described in the previous researches. It is not possible to offer an adequate description of the resonance line present in the experimental spectra of about 2.4 mm/s at 25 °C (or 2.6 mm/s at -195 °C) without involving the indicated sub-subspectra. These iron-containing components are minor in the sample under study, which does not allow us to determine their Mössbauer parameters with a high degree of reliability. But, with a high degree of certainty, Spectra $9^{\#}$ and $10^{\#}$ are related to $Fe^{2.5+}$ and Fe^{2+} in an octahedral environment [64]. A significant quadruple splitting indicates that these octahedra are much distorted, which can be realized in minerals with a layered structure.

Results of the Mössbauer spectroscopy performed on the 700 °C-dehydroxylated bauxite (Fig. 4) confirmed the above stated conclusions. All iron oxo/hydroxo-compounds decomposed to alumohematite as presented by Subspectra $1^{\#}-3^{\#}$ (Group I, Table 3). The final phase formation was not revealed on the spectra due to the kinetic factor (roasting was performed for not longer than



Fig. 4 Mössbauer absorption spectra at 25 and -195 °C of Severoonezhsk bauxite subjected to roasting at 700 °C for 60 min

Table 3 Parameters of Mössbauer spectra measured for 700 °C-roasted Severoonezhsk bauxite

Sub-			25 °C						−195 °C					
spectrum No.	Group	Phase	δ	$\Delta(=2\varepsilon)/(\mathrm{mm\cdot s}^{-1})$	Γ_{exp}	$\frac{H_{\rm eff}}{(10^7{\rm A}{\cdot}{\rm m}^{-1})}$	<i>S</i> /%	δ	$\Delta (=2\varepsilon)/(\mathrm{mm}\cdot\mathrm{s}^{-1})$	$\Gamma_{\rm exp}$	$H_{\rm eff}/(10^7{\rm A}{\cdot}{\rm m}^{-1})$	S/%		
1#			0.37	-0.21	0.27	4.1104	19.3	0.48	-0.20	0.27	4.2440	46		
2#			0.37	-0.22	0.28	4.0312	16	0.48	-0.21	0.27	4.1656	23		
3#	т	α (Eq. A1) O	0.37	-0.22	0.33	3.9296	11	0.46	-0.21	0.56	4.0320	16		
4#	1	α -($\Gamma e_{1-x}AI_x$) ₂ O ₃	0.36	-0.20	0.45	3.7872	8	_	_	_	_	_		
5#			0.36	-0.18	1.10	3.5440	11	_	_	-	_	_		
6#			0.68	-0.15	6.2	2.2480	20.5	_	_	_	_	_		
7#	V	Fe ³⁺ _{Td}	0.19	1.54	0.64	_	5.1	0.34	1.44	1.56	_	13.0		
8#	v	Fe ³⁺ _{Oh}	0.29	0.71	0.48	_	6.5	0.41	0.89	0.30	_	1.4		
9 [#]	IV	Fe_{Td}^{2+}	0.94	1.39	0.45	_	2.2	1.10	1.72	0.30	_	1.1		

60 min), which was the reason for the broadened resonance lines. On the other hand, the paramagnetic component in the central region of the spectrum (Fig. 4) included three subspectra: Subspectra $7^{\#}$ and $9^{\#}$ (Table 3) were related to Fe³⁺ and Fe²⁺, respectively, in their tetrahedral oxygen environment, while Subspectrum 8[#] was related to Fe^{3+} in its octahedral oxygen environment [64]. An increase in the area and quadruple splitting of one of the sub-subspectra of Group V (Table 3) indicates that they belong to the finely dispersed products of thermolysis of the initial sample in the superparamagnetic state.

3.3 SEM observation

To confirm the mineral composition of the

Severoonezhsk bauxite analyzed by Mössbauer spectroscopy, the SEM imaging of the particulate bauxite was performed. As the SEM-scans revealed, the major bauxite-comprising minerals of gibbsite, boehmite, and kaolinite served as the carrier-matrix for other minor mineral phases.

Figure 5 shows SEM images of the particulate iron oxide, Cr-based spinel, potassium aluminosilicate, and titanium oxide. The results of elemental analysis are listed in Table 4. It can be seen from Fig. 5(a), the particle morphology of alumohematite differed from that of spinel as the surface of alumohematite was loose and contained a plurality of voids (Fig. 5(a)); on the other hand, the chromite particles had smooth surfaces. Particles of muscovite (Fig. 5(c)) and anatase (Fig. 5(d)) both



Fig. 5 SEM images of Cr-, Fe- and Ti-containing minerals in Severoonezhsk bauxite (Red arrows locate SEM-EDX analysis points)

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Spectrum No. in Fig. 5	0	Cr	Fe	Al	Zn	Si	Mg	Ti	Κ	Phase [*]
1	44.8	27.8	10.5	6.1	5.8	0.4	_	0.3	_	Cr–Fe
2	38.6	0.6	56.1	2.1	_	1.8	_	0.4	_	Fe
3	46.0	23.4	18.3	9.7	_	0.3	1.2	1.1	_	Cr–Fe
4	58.7	-	0.9	16.4	-	17.2	0.8	0.4	5.6	Mu
5	53.4	_	9.3	2.1	_	0.6	_	31.3	_	An

Table 4 Elemental compositions of bauxite particles (wt.%)

* Cr-Fe-Chromite; Fe-Alumohematite or alumogoethite; Mu-Muscovite; An-Anatase

had smooth topology and might have been contaminated with sub-micron deposits of zinc (Zn), magnesium (Mg), and titanium (Ti) (Table 4). In Severoonezhsk bauxite, the iron in oxidation states of +3 and +2 is included, both of which are found in individual iron-containing minerals: alumohematite, alumogoethite and chromite, as well as in muscovite and anatase.

3.4 Hydrochloric leaching results of iron from bauxite

This research is the part of a series of studies aiming to develop a facile and cost-effective hydrometallurgical method for deironization of the Severoonezhsk bauxite. The suggested process includes (Fig. 1): leaching of bauxite by HCl, iron concentration from Fe-Cl liquor by solvent extraction, HCl regeneration, and pyrohydrolysis of iron concentrated solutions to obtain the hematite powder. The by-leaching residual amounts of Al are tolerated as necessary losses in this proposed process, with the fact in mind that the HCl-leached AlCl₃ would act as an effective salting-out agent in the subsequent solvent extraction of iron from acid liquor [65]. The present study emphasized on the HCl leaching of the Severoonezhsk bauxite as the central stage of the emulated deironization technology. The proposed chemical mechanism of the HCl leaching process could be summarized by the following reactions [66,67]:

 $AlOOH(s)+3HCl(l)=AlCl_3(aq)+2H_2O(l)$ (9)

$$Al(OH)_3(s)+3HCl(l)=AlCl_3(aq)+3H_2O(l)$$
(10)

$$Al_{2}(Si_{2}O_{5})(OH)_{4}(s)+6HCl(l)=2AlCl_{3}(aq)+2SiO_{2}(s)+5H_{2}O(l)$$
(11)

$$KAl_2(AlSi_3O_{10})(OH)_2(s)+10HCl(l)=$$

$$3AlCl_3(aq)+KCl(aq)+3SiO_2(s)+6H_2O(l)$$
 (12)

$$Fe_2O_3(s)+6HCl(l)=2FeCl_3(aq)+3H_2O(l)$$
 (13)

$$FeOOH(s)+3HCl(l)=FeCl_3(aq)+2H_2O(l)$$
(14)

$$FeCr_2O_4(s)+8HCl(l)=$$

$$FeCl_2(aq)+2CrCl_3(aq)+4H_2O(l)$$
(15)

$$TiO_2 + 2HCl(l) = TiOCl_2(aq) + H_2O(l)$$
(16)

$$CaSO_{4} \cdot 2H_{2}O(s) + 2HCl(l) = CaCl_{2}(aq) + 2H_{2}O(l) + H_{2}SO_{4}(l)$$
(17)

The impact of such process parameters as the temperature of extraction, HCl concentration, and S/L ratio on the degree of iron extraction is shown in Fig. 6. It could be observed that continuous increase of the process temperature from 80 to 100 °C by every 5 °C led to an increase in the iron extraction efficiency from 58.0% to 82.5% by every 5%-10% (Fig. 6(a)). We also demonstrated that an increase of the HCl concentration in situ from 51 to 77 g/L led to an increase in the degree of iron extraction from 54% to 70%, respectively (Fig. 6(b)). By further increasing the HCl concentration in the reaction medium to 161 g/L we boosted the efficiency of iron extraction up to 90%. At the S/L ratio of 1:12, the iron extraction degree reached 85% (Fig. 6(c)).

Since our study partly covered the acid technology for alumina production, it was necessary to minimize the loss of aluminum during the HCl leaching. As can be seen from Fig. 7(a), an increase of the extraction temperature from 80 to 95 °C resulted in the aluminum extraction increased by 2.5%. As in the case with the aluminum extraction, gradual concentration increase of the feed HCl solution from 105 to 132 g/L and further to 161 g/L led to a sharply increased aluminum extraction from 4.5% up to 6% and 7%, respectively (Fig. 7(b)). Inversely, a gradual decrease of the S/L ratio from 1:4 to 1:12 allowed for aluminum extraction from 3% to 6% (Fig. 7(c)). As can be concluded from the data obtained, the following technological parameters corresponded and could be used to maintain the highest iron extraction efficiency and at the same time minimizing the aluminum losses:



Fig. 6 Impact of technological parameters on iron extraction from Severoonezhsk bauxite: (a) Temperature; (b) HCl concentration; (c) S/L ratio

100 °C, C_{HCI} =105 g/L, S/L ratio of 1:12 and duration of 60 min.

3.5 HCl leaching kinetics behavior

The obtained experimental data were fitted using the well-known equations of the shrinking core model (SCM), which determined the limiting stage of the leaching process, as referred to the matching type of the kinetic curves [68,69]. The following equations were used in this study:

$$1 - (1 - X)^{1/3} = k_1 t \tag{18}$$

$$1 - \frac{2}{3X} - (1 - X)^{\frac{2}{3}} = k_2 t \tag{19}$$



Fig. 7 Effect of technological parameters of HCl leaching on aluminum extraction from Severoonezhsk bauxite: (a) Temperature; (b) HCl concentration; (c) S/L ratio

where X is the rate of Fe leaching; k_i is the apparent leaching rate constant; t is the leaching time.

Equation (18) is applicable to the leaching process limited by the chemical reaction, whereas Eq. (19) describes the processes limited by internal diffusion. DICKINSON and HEAL [70] proposed a new modification of the SCM (NSCM) as preferable for describing the kinetics of leaching processes controlled by the interfacial transfer and diffusion through the product layer:

$$\frac{1}{3\ln(1-X) + (1-X)^{-1/3} - 1 = k_3 t}$$
(20)

The experimental kinetic data from the leaching curves in Fig. 6(a) were fitted into the above models (Eqs. (18)–(20)), and the correlation coefficient (R^2) was determined. The correlation coefficient showed the deviation of the experimental data from the ideal straight curve for different SCM models. Results of the mathematical modelling of the HCl-extraction of iron are presented in Fig. 8.

As is seen from both the model-data distributions and the corresponding R^2 values in Fig. 8(a), Eq. (18) agreed more accurately with the



Fig. 8 Results of fitting of experimental kinetics data into SCM model using different equations: (a) Eq. (18); (b) Eq. (19); (c) Eq. (20)

empirical data obtained at leaching temperatures below 90 °C, indicating that the chemical reaction itself limited the rate of leaching. The diffusionbased Eq. (19) showed a lower degree of correlation with the experimental results compared to the kinetic equation for low temperatures (Fig. 8(b)). On the other hand, the NSCM Eq. (20) provided a more reliable fit to the empirical data collected at leaching temperatures above 90 °C, which pointed to the potential change in the leaching mechanism (Fig. 8(c)). At the leaching temperatures of 90 °C and higher, the limiting stage could become the interfacial transfer and diffusion through the product layer or the unreacted matter, presented by the Al-minerals, not dissolved in HCl.

The NSCM Eq. (20) reliably fitted the experimental data over the 80–100 °C span of the tested leaching temperatures, and was the mathematical model of choice used to further evaluate the activation energy (E_a) of the chemical reaction limiting the HCl leaching of the Severoonezhsk bauxite. To calculate the E_a , ln k as function of T^{-1} was plotted, where k was the reaction rate constant represented by the slope of each kinetic curve resulted from inserting the experimental data into Eq. (20), and T is the temperature. Figure 9 depicts the ln k as a function of the inverse temperature of the HCl-deironization.



Fig. 9 ln $k-T^{-1}$ relationship drawn for NSCM-fitted experimental HCl leaching data

The reaction rate constant can be described by the Arrhenius equation:

$$k = k_0 \exp\left[-E_a/(RT)\right] \tag{21}$$

where k_0 is the pre-exponential factor, min⁻¹; *T* is the reaction temperature, K; and *R* is the mole gas constant, 8.314 J/(mol·K).

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Linear fitting of the Arrhenius plot (Fig. 9) showed the temperature sensitivity of the E_a of the bauxite HCl-leaching, as evidenced by a clear curve break at 90 °C with the two linear components corresponding to the low (blue line, Fig. 9) and high (red line, Fig. 9) activation energies. Therefore, two E_a values could be calculated according to Eq. (21). In the high temperature range of 90–100°C, the activation energy was 37.845 kJ/mol, which corresponded to the diffusion stage. In the low temperature range of 80–90 °C, the activation energy was 54.506 kJ/mol, outlining the chemical reaction as the limiting stage.

The effects of the HCl concentration and S/L ratio on the iron leaching kinetics were analyzed using Eq. (20) and graphically depicted on Figs. 10 (a, b) and 11(a, b), respectively. From this data the dependence $\ln k - \ln C_{\rm HCl}$ can be constructed to determine the empirical order of the reaction in regard to the HCl concentration, and the $\ln k - \ln \varepsilon_{\rm S/L}$ ($\varepsilon_{\rm S/L}$ is the S/L ratio) relationship in regard to the S/L ratio (see Figs. 6(b,c)).

As a result of fitting the experimental data from Figs. 10(a, b) into a linear dependence, the empirical reaction order for $C_{\rm HCl}$ is calculated to be 2.07. The empirical reaction order for the S/L ratio was calculated to be -1.01. By substituting Eq. (21) into Eq. (20), the following equation could be obtained:

$$1/3\ln(1-X) + (1-X)^{-1/3} - 1 = k_0 \exp[-E_a/(RT)] \cdot t$$
 (22)

where k_0 is dependent on the initial process parameters, including the initial C_{HCI} and S/L ratio, and the reaction time. Equation (22) could be rewritten as follows:

$$\frac{1}{3}\ln(1-X) + (1-X)^{-1/3} - 1 = k_0 C_{\text{HCl}}^{n_1} \varepsilon_{\text{S/L}}^{n_2} \exp[-E_a/(RT)] \cdot t$$
(23)

where n_1 is the reaction order of the C_{HCl} ; n_2 is the order of the S/L ratio. Based on the results calculated in the present section of our study (see Figs. 9–11), the HCl leaching of Fe from the Severoonezhsk bauxite in the temperature range of 90–100 °C could then be described by the following equation:



Fig. 10 Impact of C_{HCl} on kinetics of HCl leaching of iron from Severoonezhsk bauxite: (a) HCl leaching rates calculus via NSCM at various C_{HCl} ; (b) Relationship between $\ln k$ -ln C_{HCl}



Fig. 11 Impact of S/L ratio ($\varepsilon_{S/L}$) on kinetics of HCl leaching of iron from Severoonezhsk bauxite: (a) HCl leaching rates calculus via NSCM at various S/L ratios; (b) Relationship between ln k-ln $\varepsilon_{S/L}$

$$\frac{1/3\ln(1-X) + (1-X)^{-1/3} - 1}{k_0 C_{\text{HCl}}^{2.07} \varepsilon_{\text{S/L}}^{-1.01} \exp[-37845/(RT)] \cdot t}$$
(24)

Figure 12 shows the plot of the left part of Eq. (24) vs $C_{\text{HCl}}^{2.07} \varepsilon_{\text{S/L}}^{-1.01} \exp[-37845/(RT)] \cdot t$, from which the value of k_0 could be determined.



Fig. 12 Relationship between $1/3\ln(1-X)+(1-X)^{-1/3}-1$ and $C_{\text{HCI}}^{2.07} \varepsilon_{\text{S/L}}^{-1.01} \exp[-37845/(RT)] \cdot t$ for iron extraction

Despite the negligible scattering, the calculated data could be fitted by the straight curve with the correlation coefficient of R^2 =0.993 and the slope of this line corresponding to k_0 , from which the k_0 value of 0.0036 min⁻¹ could be derived. The substitution of calculated values into Eq. (24) resulted in the final semi-empirical Eq. (25) to describe the overall HCl-leaching of iron:

$$\frac{1/3\ln(1-X) + (1-X)^{-1/3} - 1}{0.0036 C_{\text{HCI}}^{2.07} \varepsilon_{\text{S/L}}^{-1.01} \exp[-37845/(RT)] \cdot t}$$
(25)

3.6 Charicterization of HCl-leached Severoonezhsk bauxite

Chemical composition of the HCl-liquor obtained at the above optimized technological parameters of the leaching process (100 °C; C_{HCI} = 105 g/L; $\varepsilon_{S/L}=1:10$; t=60 min) was examined by ICP-OES (in g/L): Fe, 7.03; Al, 2.35; Ca, 0.65; Cr, 0.33. The content of rare-earth metals in the liquor was as follows (in mg/L): Sc, 6.1; Ce, 5.6; Ga, 2.1, with the corresponding extraction rates of 60%, 45%, and 33%, respectively. The degree of Ga extraction as low as 33% could be explained by the fact that Ga was mainly intercalated into silicon oxide or aluminosilicates, not prone to the HCl-dissolution, therefore, most of it retained in the solid residue after leaching [71]. The TEM imaging located the presence of Sc in the raw bauxite (Fig. 13). The TEM images showed that the

particulate aluminosilicate contained iron along with trace amount of Sc, both engrained in the surfaces of the aluminosilicate particles (Fig. 13(a)). This was in agreement with the previous researches that showed a direct correlation between the amounts of Sc and goethite or hematite [72,73]. The raw bauxite also contained calcium carbonate particles sized 1–10 μ m with trace inclusions of Sc (Fig. 13(b)). Association of rare earth metals with carbonate minerals is also possible [74].

Chemical composition of the bauxite residue after HCl leaching is listed in Table 5. The ICP-OES data showed that as an effect of HCl leaching, the iron oxide content of the Severoonezhsk bauxite was reduced by less than 1 wt.%, the chromium oxide content was notably reduced from 0.86 to 0.24 wt.%, and calcium oxide was cleaved to the trace amount of 0.04 wt.%. The $\mu_{\rm Si}$ of the bauxite residue decreased to 1.74. The XRD patterns recorded for the bauxite residue after HCl leaching confirmed the complete dissolution of gypsum, goethite, and hematite from the raw bauxite (Fig. 14). The gibbsite phase preserved in the bauxite after HCl leaching as identified by the sharp peaks on the XRD patterns, intensity of the gibbsite peaks decreased by 50% as compared to the raw bauxite. The XRD scans of bauxite residue identified sharp peaks of two aluminosilicates: kaolinite and muscovite, which appeared in place of the Fe-peaks, as compared to the XRD patterns of raw bauxite.

3.7 Mössbauer analysis results of bauxite solid residue

The Mössbauer spectra of the HCl-leached bauxite residue were measured at room temperature (Fig. 15) and predominantly contained three resonance lines. A wide singlet with an isomeric shift of 0.36 mm/s and relative area of 48% (Table 6, Subspectrum $1^{\#}$, 25 °C) could conditionally indicate the relaxation nature of the wide and extended absorption background. This part of the spectrum resolved more sharply at -195 °C and could be described by a superposition of two sextets (Table 6, $1^{\#}-3^{\#}$), the subspectra of which could be attributed to the Al-mineral traces detected in the raw bauxite (Table 2) as Groups II and III. The traces of the alumohematite still presented in the residue after the alumoakageneite full HCl-leach out.



Fig. 13 TEM images and EDX elemental mapping of aluminosilicate particle with Fe (a) and calcium carbonate particle (b)

Table 5 Chemical composition of bauxite residue by ICP-OES after HCl leaching at 100 °C, C_{HCl} =105 g/L, $\varepsilon_{\text{S/L}}$ =1:10 and 60 min (wt.%)

Al_2O_3	SiO_2	Fe_2O_3	TiO ₂	CaO
53.83	30.89	0.84	3.10	0.04
Cr ₂ O ₃	LOI [*]	Sc**	Ga ^{**}	Ce ^{**}
0.24	11.06	50	50	80

* Loss on ignition at 1000 °C; ** in mg/kg

The central parts of the Mössbauer spectra measured at both 25 and $-195 \,^{\circ}\text{C}$ could be described by the superposition of three doublets corresponding to the iron atoms Fe³⁺, Fe^{2.5+}, and Fe²⁺ (Table 6, Subspectra 3[#]-5[#], respectively) in the octahedral oxygen environment [64]. The last two subspectra listed in Table 6, and specifically, Subspectra 4[#] and 5[#], exhibited a strong temperature dependence of their quadruple splitting, which is commonly featured in the high-spin state of Fe²⁺ [75]. The parameters calculated for the



Fig. 14 XRD patterns of raw bauxite and bauxite residue after HCl leaching at 100 °C, $C_{\text{HCl}}=105$ g/L, $\varepsilon_{\text{S/L}}=1:10$ and 60 min

mentioned subspectra were in a good agreement with the parameters of the subspectra of Groups III and IV of the crude Severoonezhsk bauxite (Table 2) and attributed the iron atoms to the same mineral phases.



Fig. 15 Mössbauer spectra of Severoonezhsk bauxite residue after HCl leaching at 25 and -195 °C

Sub-				25 °	С		−195 °C					
spectrum No.	Group	Phase	δ	$\Delta(=2\varepsilon)/$ (mm·s ⁻¹)	$\Gamma_{\rm exp}$	S/ %	δ	$\Delta(=2\varepsilon)/(\mathrm{mm\cdot s}^{-1})$	$\Gamma_{\rm exp}$	$H_{\rm eff}/(10^7{\rm A}{\cdot}{\rm m}^{-1})$	S/ %	
$1^{\#}$	II	α -Fe _{1-x} Al _x OOH	0.36	_	10.04	48	0.45	-0.11	2.0	501	30	
$2^{\#}$	ш	$\rho = 100000000000000000000000000000000000$	0.36	_	10.04	48	0.78	-0.22	1.3	281	10.1	
3#	111	p -r e_{1-x} AI _x O(On,CI)	0.34	0.63	0.46	33.6	0.46	0.66	0.50	_	38.0	
4#	П/	$Fe_{Oh}^{2.5+}$	0.61	1.68	1.17	11.4	0.65	2.24	1.0	_	10	
5#	1V	Fe_{Oh}^{2+}	1.10	2.57	0.39	6.6	1.24	2.73	0.38	_	12.1	

 Table 6 Mössbauer spectra parameters of Severoonezhsk bauxite residue after HCl leaching

Mössbauer parameters for chromite-type minerals vary over a wide range of values depending on their origin, stoichiometry, the presence of impurities, etc [76,77]. The combination of Subspectra $3^{\#}-5^{\#}$ can be related to chromite, since a similar combination of subspectra may apply to spinel type minerals.

As expected, Mössbauer spectroscopy of the post-thermolysis bauxite residue after HCl leaching (Fig. 16) revealed that as a result of the 700 °C airroasting, the alumogoethite and alumo- akaganeite (Subspectra 1[#] and 2[#], Table 6) decomposed into alumohematite [78], which was shown by Subspectra 1[#]-3[#] (Table 7). The iron represented in the bauxite residue in the paramagnetic form (Subspectra 3[#]-5[#], Table 6), was oxidized into the Fe³⁺-compounds (Subspectra 3[#] and 4[#], Table 7) in the octahedral oxygen environment [64]. In both cases, given the significant width of the resonance lines and the magnitude of the quadrupole splitting of the doublets, the formation of the corresponding Fe-phases at 700 °C and air atmosphere was

incomplete, and indicated the presence of Fe-phases dispersed over the sample as ultrafine nanoparticles with low crystallinity and inhomogeneous local environments of iron atoms.

3.8 SEM images of bauxite residue after HCl leaching

The mineral composition of the bauxite residue after leaching was further confirmed by SEM imaging. As analyzed on the SEM images bauxite solid residues (Fig. 17), contained sub-micron particulate goethite or hematite, as well as the individual chromite particles, which varied in size from 10 to 20 µm (Fig. 17(a)). The particulate chromite contained the inclusions of zinc and manganese (Table 8). The EDX mapping identified the residual Fe-inclusions in muscovite particles to be uniformly distributed throughout the surface of the entire individual particle (Fig. 17(b)) and accounting for 1.0-2.5 wt.% of muscovite. The elemental compositions of examined particles are shown in Table 8.



Fig. 16 Mössbauer spectra of Severoonezhsk bauxite residue after HCl leaching and then roasting at 700 °C

Table 7 Mössbauer spectra parameters of HCl-leached (25 °C) Severoonezhsk bauxite solid residue subjected to roasting at 700 °C

Subspectrum No.	Group	Phase	δ	$\Delta(=2\varepsilon)/(\mathrm{mm\cdot s}^{-1})$	$\Gamma_{\rm exp}$	$H_{\rm eff}/(10^7{\rm A}{\cdot}{\rm m}^{-1})$	<i>S</i> /%
1#			0.36	-0.22	0.61	4.0560	9
$2^{\#}$	Ι	α -(Fe _{1-x} Al _x) ₂ O ₃	0.33	-0.32	1.9	3.5040	12
3#			0.33	-0.32	4.6	1.5520	29
4#	V/I	E - ³⁺	0.33	1.38	1.08	_	28
5#	V1	re _{Oh}	0.31	0.72	0.56	_	23



Fig. 17 SEM images of chromite particles (a) and muscovite particles (b) (Red arrows indicate points of SEM-EDX analysis application)

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1		1	(/						
Spectrum No. in Fig. 17	0	Cr	Fe	Al	Zn	Si	Mn	Ti	Κ	Phase*
6#	36.7	33.6	11.8	6.8	3.7	0.3	1.1	0.3	_	Cr–Fe
$7^{\#}$	58.5	_	2.5	16.7	_	16.0	_	1.1	4.4	Mu

Table 8 Elemental compositions of bauxite particles (wt.%)

* Cr-Fe-Chromite; Mu-Muscovite

Summarizing the obtained SEM data, it can be concluded that the iron remaining in HCl-leached bauxite residue was concentrated in refractory particles of chromite and muscovite. The minerals poorly dissolved even by the acidic blends [79] and under mechanical activation [80]. As an additional facilitation of the HCl leaching technology, we discovered that the obtained Fe-chloride liquor has the following element contents (in g/L): Fe, 5.45; Al, 2.25; Ca, 0.40; Cr, 0.16; Ti, 0.06; Sc, 6.8×10^{-3} ; Ce, 4.1×10^{-3} ; Ga, 2.3×10^{-3} . So, it could be further directed to the extraction of Sc, Ce, and Ga.

4 Conclusions

(1) The experimental analysis via XRD and Mössbauer spectroscopy, coupled with SEMimaging, established alumogoethite, alumohematite, alumoakaganeite, and chromite as the Fe-containing minerals located in bauxite. The inclusions of iron impurities were found in muscovite and anatase phases of the Severoonezhsk bauxite.

(2) The following technological parameters of HCl leaching of iron from the Severoonezhsk bauxite were experimentally optimized: 100 °C, $C_{\rm HCl}$ =105 g/L, S/L ratio 1:10, and 60 min. The optimized HCl leaching setup reached the Fe extraction of 82.5%, with aluminum loss kept at levels as low as 4.5%.

(3) The kinetic behaviors of the iron leaching process were evaluated using the shrinking core models, and semi-empirical equation was theoretically tailored to describe the deironization process as a function of the HCl concentration, S/L ratio and temperature as follows: $1/3\ln(1-X)+(1-X)^{-1/3}-1=0.0036 C_{\rm HCl}^{2.07} \varepsilon_{\rm S/L}^{-1.01} \exp[-37845/(RT)] \cdot t.$

(4) As a result of HCl leaching, the alumohematite was found to completely dissolve from the Severoonezhsk bauxite. The developed HCl leaching method left trace amounts of alumogoethite and alumoakaganeite in the bauxite residues. Most of the Fe-inclusions in the bauxite residue were present in refractory minerals chromite and muscovite.

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从勃姆石-高岭石型高硅铝土矿中 盐酸浸出铁的机理与动力学

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摘 要:利用 XRD、ICP-OES、TG/DSC、SEM、TEM 和穆斯堡尔(Mössbauer)光谱研究来自俄罗斯阿尔汉格尔斯 克地区 Severoonezhsk 铝矿中铝土矿的化学和矿物组成,发现该铝土矿的含铁矿物包括铝针铁矿(*a*-Fe_{1-x}Al_xOOH)、 铝赤铁矿(*a*-(Fe_{1-x}Al_x)₂O₃)、正方铝针铁矿(β-Fe_{1-x}Al_xO(OH,Cl))和铬铁矿(FeCr₂O₄)。在温度为 100 °C、HCl 浓度为 10%,固液比为 1:10 及浸出时间为 60 min 的条件下,盐酸浸出铝土矿的铁浸出率为 82.5%,而铝的损失不到铝土 矿中总铝含量的 4.5%。铁浸出过程的动力学分析表明,温度为 90~100 °C 时,扩散是浸出过程的速率限制环节。 铝土矿浸出渣含有微量的 *a*-Fe_{1-x}Al_xOOH 和 β-Fe_{1-x}Al_xO(OH,Cl),大部分铁呈 FeCr₂O₄ 形态。除铁氧化物外,铝土 矿盐酸浸出渣中铬和钙氧化物的含量也显著降低。含氯化铁的浸出液含有稀土元素(REE): 6.8 mg/L Sc、4.1 mg/L Ce 和 2.3 mg/L Ga。

关键词:铝土矿;酸浸;铁提取;动力学;穆斯堡尔光谱

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