Article

Solvent Extraction of Iron(III) from Al Chloride Solution of Bauxite HCl Leaching by Mixture of Aliphatic Alcohol and Ketone

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Abstract: Research into the solvent extraction of iron(III) from a chloride solution after bauxite HCl leaching by neutral oxygen-containing extractants and their mixtures were studied and the iron(III) extraction degree from chloride solutions using alcohols is presented. The effect of dilution of alcohol with a ketone by an extraction mixture in relation to its effectiveness was investigated. The iron(III) was efficiently extracted by the mixture of 1-octanol and 1-decanol (70%) with 2-undecanone (30%) from hydrochloric bauxite leach liquor at an O:A ratio = 2-4:1 at an iron(III) concentration of 7.4 g/L and 6 M HCl. For the removal of iron-containing organic phase from impurities (Al, Ca, Cr) that are co-extracted with iron(III), we used two step scrubbing at O:A = 5:1 by 7 M HCl as a scrub solution. The iron(III) stripping at the O:A ratio is shown. Using counter-current cascade of extractors, it was possible to obtain an $FeCl_3$ solution with the iron(III) content of 90.5 g/L and total impurities less than 50 mg/L.

Keywords: solvent extraction; bauxite; iron; aluminum; chloride solution; alcohol; ketone

1. Introduction

Iron oxide (Fe_2O_3), along with silica (SiO_2), is the main impurity in the alumina production industry. When using alkali methods (Bayer, sintering), iron remains in an alkali-insoluble residue-red mud [1,2]. To extract Fe_2O_3 in a separate fraction, hydrothermal treatment with the addition of $FeSO_4$ is used [3]. Another method involves the use of bauxite sinter after calcination with calcium carbonate ($CaCO_3$) to further alkali leaching with the addition of Fe^{2+} to convert non-magnetic iron to magnetite (Fe_3O_4) [4]. The reduction roasting method at 600 °C is used to process high-iron bauxite ($Fe_2O_3 > 20$ wt. %) and obtain magnetite (Fe_3O_4). Furthermore, it separates from the bauxite sinter by magnetic separation [5,6].

For high-silica Al-containing ores with a silica ratio <3 (mass ratio of Al_2O_3 to SiO_2), the hydrochloric acid (HCl) method is the most relevant for further alumina production [7,8]. In this case, silica practically does not react with HCl, but the iron oxide is almost completely leached into the solution. Al is mainly presented in aluminosilicates as kaolinite ($Al_2Si_2O_5(OH)_4$), muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), or boehmite (AlOOH). High-pressure reactors must be used to leach these minerals [9]. Iron is primarily present in bauxite in oxides: hematite (Fe_2O_3) and goethite (FeOOH). Thus, using a hydrochloric acid, it is possible to leach more than 90% of iron at atmospheric pressure using the difference in iron and aluminum mineral reactivity [10]. For the concentration of iron into a separate solution and the possibility of reusing HCl, the most relevant is the solvent extraction method.

For iron solvent extraction, organophosphorus extractants are mainly used, the most popular of them is tri-n-butyl phosphate (TBP). TBP practically does not extract iron(II) [11];

however, it is an effective extractant for the iron(III) extraction from hydrochloric solutions (HCl) [12–14].

Mishra et al. [15] carried out a comparative analysis of the Cyanex class extractants: Cyanex 921 (trioctylphosphine oxide) and Cyanex 923 (a mixture of tertiary octyl- and hexylphosphine oxides) with TBP for iron extraction. Distilled kerosene and 2-ethylhexanol were used as the solvent and modifier. The influence of the HCl, H^+, Cl^- concentration, and the extractant on the iron(III) extraction degree had been studied. With an increase in the HCl concentration from 0.78 M to 9.29 M, the extraction degree increased from 49.8% to 99.8% for Cyanex 921, from 54.1% to 99.9% for Cyanex 923, and from 13.6% to 99.7% for TBP. With an increase in the Cl^- concentration from 4.58 to 6.08 M at $[H^+]$ = 4.58 M, the iron(III) extraction degree increased from 64.7% to 84.9% (Cyanex 921), from 66.0% to 86.4% (Cyanex 923), and from 7.9 to 44.1% (TBP). It was found that the efficiency of extractants for the iron(III) extraction increased in the following order: TBP < Cyanex 921 < Cyanex 923.

Cui et al. [16,17] studied the extraction of iron(III) from HCl by extractants *N,N,N′,N′*-tetrabutylmalonamide (TBMA) and *N,N,N′,N′*-tetrabutyl-3β-hydroxyglutaramide (TBDGA). The extraction results were compared with those of *N,N,N′,N′*-tetrabutylsuccinamide (TBSA) to understand the relationship between the chemical structure of the extractants and the iron(III) extraction degree. It was found that, according to the extraction ability to iron(III), the extractants were arranged in the following order: TBMA < TBSA < TBDGA. The use of *N,N,N′,N′*-tetra-2-ethylhexyldiglycoliamide (T2EHDGA) in various solvents has also been studied. In this case, the distribution coefficient of iron(III), depending on the HCl concentration changing, were increased in the order: toluene < n-hexane < n-octane < n-dodecane [18].

Tertiary amines [19,20] and imines [21] are also effective for the extraction of iron(III) from chloride solutions. Quaternary ammonium bases, for example, Aliquat 336 (a mixture of 3-octyl- and 3-decylamine chlorides) was used to extract iron(III) from a chloride solution after leaching of poor iron ores. Purified kerosene was used as a diluent, and 30% nonylphenol was used as a modifier. The growth of the HCl concentration from 1.67 to 9.77 increased the iron(III) extraction degree from 51% to 97%. The salting-out ability of sodium salts at C(HCl) = 2 M increased in the order: $Na_3C_6H_5O_7$ < CH_3COONa < $NaNO_3$ < Na_2SO_4 < NaCl [22].

Oxygen-containing reagents can be used with high efficiency in the extraction of iron(III) from chloride solutions. Mao et al. studied the extraction ability of decanol in kerosene for the iron(III) extraction from model solutions [23]. It was found that the equilibrium distribution of iron(III) between phases during extraction was obtained for 5 min, and the optimal reagent for stripping was 0.5 M HCl. Wang et al. proposed a flowsheet for ilmenite treatment, which included the iron(III) extraction by 2-octanol. The iron(III) extraction degree was 99.6% at two stages of counter-current extraction at the organic/aqueous ratio (O:A) = 1:3 and an C(HCl) = 9.35M [24].

The use of methyl isobutyl ketone (MIBK) makes it possible to obtain high-purity ferric chloride solutions ($FeCl_3$) [25]. The low flash point of 14–18 °C and high solubility in H_2O of 19 g/L complicates its application in industry [26]. There is also a possibility of iron(III) extraction by alkyl aryl ketones from both chloride and sulfate solutions [27]. To increase the extraction capacity and selectivity of extractants, it is possible to use mixtures of reagents based on TBP [28–30]: TBP and MIBK [31]. When using a mixture containing 70% TBP and 30% MIBK, the maximum extraction of iron(III) was observed.

The synergistic coefficient of mixtures of cation-exchange and neutral extractants of di(2-ethylhexyl) phosphoric acid (D2EHPA) with MIBK and TBP in kerosene was determined. It was found that a mixture of D2EHPA and MIBK in a ratio of 3:2 had the greatest synergism [32]. It was found that using a mixture of 0.16 trioctylamine (TOA) and 0.86 M decanol for iron(III) extraction from an 8 M HCl solution formed the complex compound $HFeCl_4 \cdot TOA \cdot 2decanol$, which decomposes at contact with low HCl concentration solutions that provide stripping [33].

Voshkin et al. extracted iron(III) from chloride solutions with mixtures of di(2-ethylhexyl) dithiophosphoric acid (D2EHDTPA) and trioctylmethylammonium (TOMA) at pH < 0. In this case, the iron(III) stripping reached 99% at 0.1 M H_2SO_4 [34].

The most promising extractants for the iron(III) extraction from chloride solutions are high-molecular-weight aliphatic ketones, which are used with great effect for iron purification of a nickel chloride solutions. In addition to the high selectivity of ketones to iron(III), it is possible to obtain a pure solution with a high iron(III) content at the stripping stage [35].

Thus, using ketones to extract iron(III) is a relevant method. In this research, the possibility of using a mixture of aliphatic ketone 2-undecanone with an industrial mixture of $C_8 + C_{10}$ alcohols for the iron(III) extraction from chloride solutions with an aluminum content of 2–3 g/L was investigated. The main aim was to remove iron(III) from the Al–Cl solution as selectively as possible, followed by obtaining a pure concentrated $FeCl_3$ solution. Based on the experimental data, the extraction and concentration of iron(III) from an Al–Cl solution on the 9-stage cascade of counter-current extractors were investigated. A concentrated $FeCl_3$ solution with a low content of Al, Ca, and Cr(III) was obtained.

2. Materials and Methods

2.1. Materials and Reagents

The extractants 1-octanol, 1-decanol, 2-octanone (Vekton, Moscow, Russia), technical mixture of 1-octanol and 1-decanol ($C_8 + C_{10}$) (51.9% and 47.5%, Crestmont Sdn Bhd, Sungai Buloh, Malaysia), methyl isobutyl ketone (EKOS-1, St. Petersburg, Russia), 4-heptanone, 4-nonanone (Reachem, Moscow, Russia), 2-nonanone, 2-decanone (Haihang, Jinan, China), and 2-undecanone (Treatt, Bury St Edmunds, Great Britain) were used as extractants. Dodecane (Vekton, Moscow, Russia) was used as the inert diluent. 2-octanone, MIBK, 4-heptanone, and 4-nonanone were purity grade; all other chemicals used were reagent grade. $FeCl_3 \cdot 6H_2O$ and HCl (LenReactiv, St. Petersburg, Russia) were used for the preparation of model solutions.

2.2. Analysis

Concentration of iron(III) in solution was determined by an atomic absorption spectrophotometer AAnalyst 400 (Perkin Elmer, Waltham, MA, USA). Concentration of Al, Ca, and Cr(III) in solutions were determined by an inductively coupled plasma atomic emission spectrometer ICPE-9000 (Shimadzu, Kyoto, Japan). Detection limits for all analyzed metals were found at 1 ppm. The metal concentration in the organic phase was calculated as the difference between its content in the aqueous phase before and after extraction.

2.3. Experiments

The bauxite sample was collected from Severoonezhsk Bauxite Mine (Severoonezhsk, Arkhangelsk region, Russia; 62.562530° N, 39.690204° E). After crushing, grinding, and classification to a −100 μm particle size, it was leached by 6 M HCl in a 500 mL flat bottom flask; the reaction was agitated using an IKA C-Mag HS 7 digital magnetic stirrer (IKA, Zhejiang, Hangzhou, China). The bauxite load of 50 g was admixed with 250 mL of HCl at the stirring rate in all tests maintained at 350 rpm. The HCl leaching was performed at temperatures of 80 °C. The leaching lasted for 120 min, and the solid:liquid ratio was 1:5. The chemical compositions of raw bauxite and bauxite after leaching are shown in Table 1.

Table 1. Chemical composition [wt. %] of the Severoonezhsk bauxite before and after HCl leaching.

	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	Cr_2O_3	LOI
Raw bauxite	49.26	24.18	5.56	2.94	0.88	0.86	16.02
Bauxite after HCl leaching	55.83	30.89	0.84	3.10	0.04	0.24	11.06

For solvent extraction, a certain volume of aqueous (A) and organic (O) phases were placed in a separation funnel and mixed vigorously for 5 min. After phase disengagement,

the raffinate was separated for the determination of Fe, Al, Ca, and Cr concentrations. Scrubbing of the organic phase from co-extracted impurities was carried out for 5 min. Iron stripping was carried out in a separation funnel by 0.2 M HCl solution for 5 min. After phase demixing, the aqueous phase was separated from the organic phase. All solvent extraction, scrubbing, and stripping experiments were carried out at room temperature.

The iron(III) extraction in a continuous mode was studied in a counter-current cascade of mixing-settling type extractors (Tananaev Institute of Chemistry, Apatity, Russia). The schematic of the extractor at the second stage of extraction is shown in Figure 1.
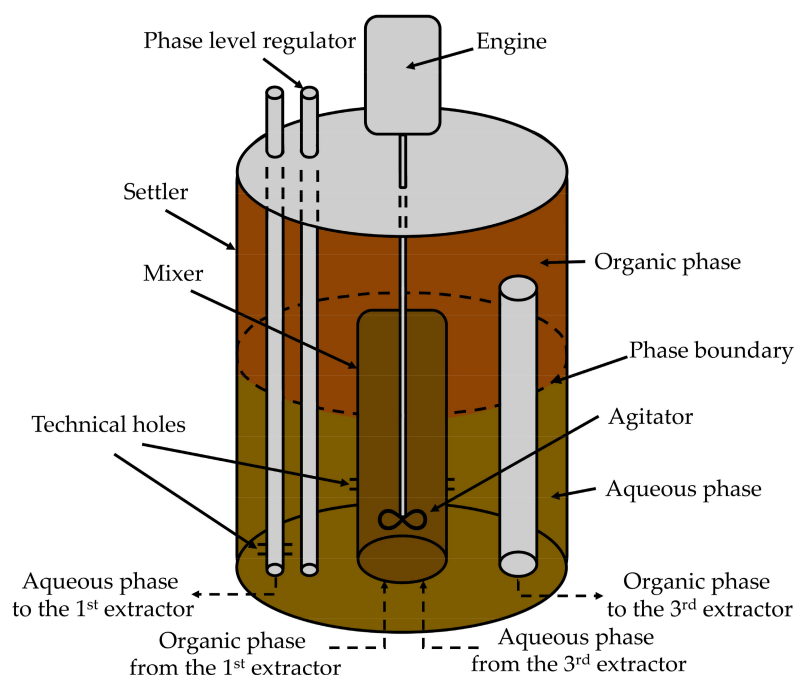
Figure 1. Scheme of mixer-settler extractor at the second stage of iron(III) extraction.

The extraction efficiency (E), distribution coefficient (D), synergistic coefficient (R), scrubbing efficiency (S_c), and stripping efficiency (S_t) were calculated with the following equations:

$$E = C_{org}/C_f \times 100\%, \tag{1}$$

$$D = C_{org}/C_r, \tag{2}$$

$$R = D_{mix}/(D_k + D_a), \tag{3}$$

$$S_c = C_{sc}/C_{org} \times 100\%, \tag{4}$$

$$S_t = C_{st}/C_{org} \times 100\%, \tag{5}$$

where C_f is the metal concentration in the feed solution before extraction, g/L; C_{org} is the metal concentration in the organic phase, g/L; C_r is the metal concentration in raffinate, g/L; D_{mix} is the distribution coefficient of the extractants mixture; D_k is the distribution coefficient of the ketone; D_a is the distribution coefficient of the alcohol; C_{sc} is the metal concentration in the scrub solution, g/L; and C_{st} is the metal concentration in the strip solution, g/L.

3. Results

3.1. Iron(III) Extraction by Neutral Oxygen-Containing Extractants from HCl Solution

For the extraction of iron(III) from a HCl solution, a comparison of the oxygen-containing organic compound extraction capacity was carried out (Figure 2). It was found that using aliphatic ketones at 6 M HCl and 10 g/L of Fe(III), the iron(III) extraction degree decreased with an increase in the length of the ketone hydrocarbon radical, but was not

less than 90%. Using aliphatic alcohols increased the iron(III) extraction degree in the order: 1-decanol < 1-octanol < C_8 + C_{10}.
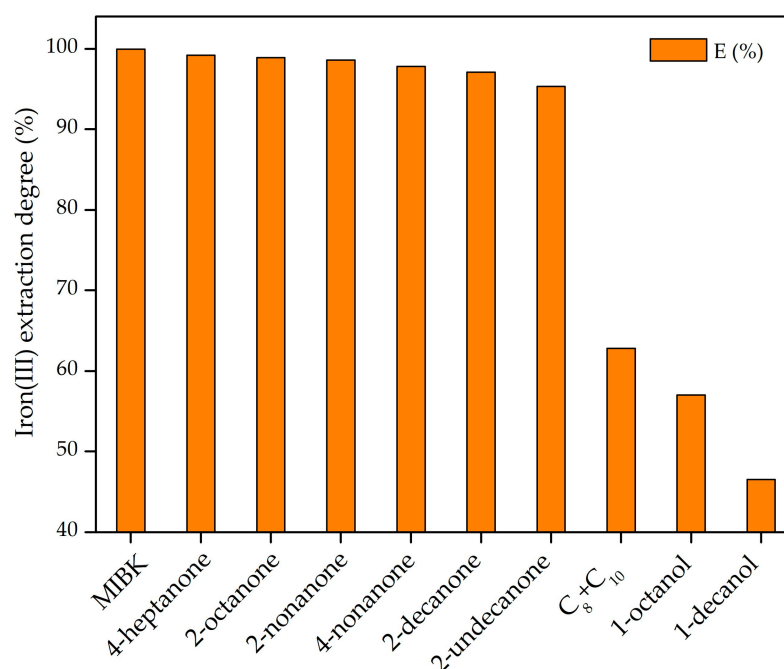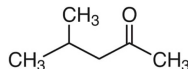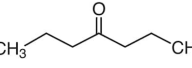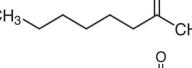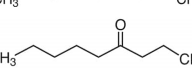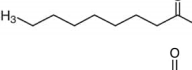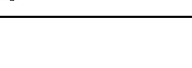

Figure 2. The dependence of iron(III) extraction degree (E) by extractant at C(HCl) = 6 M, C(Fe) = 10 g/L, O:A = 1:1.

In previous research, it was found that the extraction ability of unbranched octanol isomers increased when an inert diluent was added [36]. To continue this research, the extraction of iron(III) with mixtures based on alcohols and ketones was studied. An industrial mixture of C_8 + C_{10} aliphatic alcohols was used as the alcohol as it had the highest iron(III) extraction degree. 2-undecanone was selected as the ketone as it had the highest flash point and lowest water solubility (Table 2). The extraction degree played a lesser role than the physical properties of ketones because the E(Fe) for all studied ketones exceeded 90%.

Table 2. Ketone flash point and solubility in water [26,37].

Ketone	Molecular Formula	Structure	Flash Point, °C	Solubility in Water, g/L (25 °C)
MIBK	$C_6H_{12}O$		14–22.78	19
4-heptanone	$C_7H_{14}O$		48.89	3.2
2-octanone	$C_8H_{16}O$		51.67	0.899 (20 °C)
2-nonanone	$C_9H_{18}O$		64.44	0.371
4-nonanone	$C_9H_{18}O$		61.40	–
2-decanone	$C_{10}H_{20}O$		85.00	0.077
2-undecanone	$C_{11}H_{22}O$		88.89	0.020

3.1.1. Iron(III) Extraction by Mixtures of 2-Undecanone and C_8 + C_{10} Alcohols

The dependence of the iron(III) extraction degree from the HCl solution at 5.7 M HCl, 8.4 g/L Fe(III) by mixtures of 2-undecanone and C_8 + C_{10} alcohols was studied. It was found that the addition of 20 vol.% ketone to a mixture of alcohols increased the iron(III) extraction degree up to 91.7%, which corresponded to the value of pure 2-undecanone (Figure 3). With a further increase in the ketone concentration in alcohol, the iron(III) extraction degree also increased to 98.4% at 50–60 vol.% in the 2-undecanone concentration.
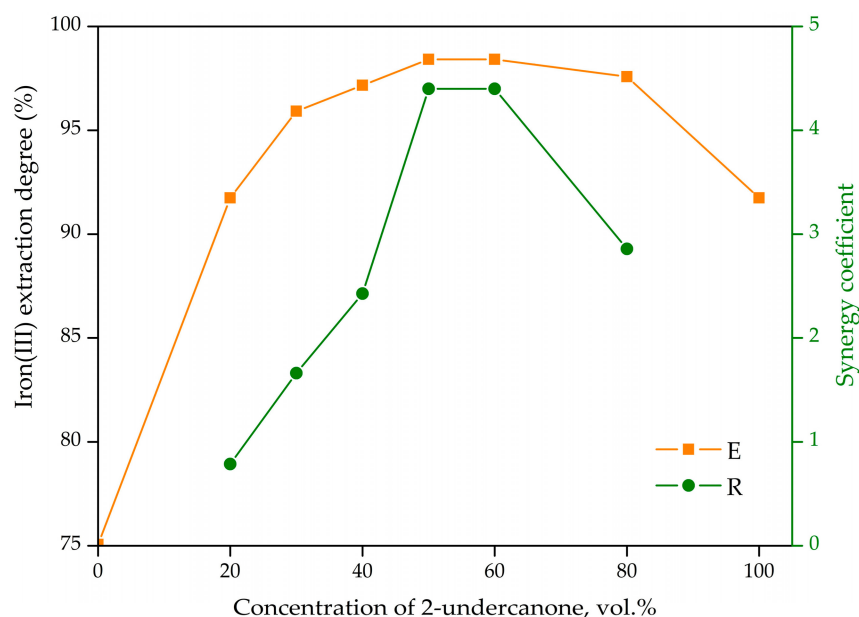

Figure 3. The dependence of iron(III) extraction degree (E) and synergy coefficient (R) on the concentration of 2-undercanone at C(HCl) = 5.7 M, C(Fe) = 8.4 g/L, O:A = 1:1.

The synergistic effect on the iron(III) extraction by mixtures of 2-undecanone and C_8 + C_{10} was determined. The addition of the 30 vol.% of ketone to alcohol increased the synergistic coefficient to 1.65, and the highest R value was 4.4 at a ketone concentration of 50–60 vol.%. The synergistic effect can be explained by an increase in excess enthalpy upon adding ketone to alcohol, which reached a maximum at a ketone:alcohol ratio of 1:1. There was the destruction of hydrogen bonds in alcohol and the formation of an intermolecular bond between the alcohol hydroxyl group and the ketone carbonyl group, which contributed to the destruction of the self-associated alcohol complex (Figure 4). With the further increase in the ketone:alcohol ratio, the alcohol concentration and its monomers decreased [38]. Thus, the addition of ketone to the alcohol promoted the weakening of the bond in the self-associated alcohol molecule with the subsequent formation of more extraction active alcohol monomers. Due to this fact, the extraction capacity of the ketone:alcohol mixture increased and the synergistic effect appeared.
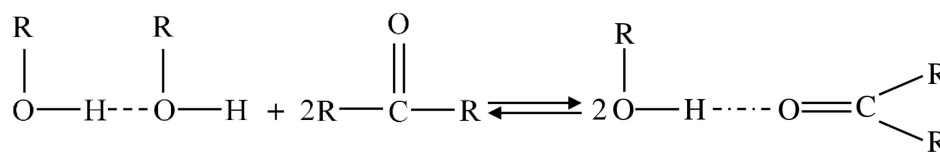

Figure 4. Schematic diagram of the destruction of the self-associated complex of alcohols by ketone. R is the hydrocarbon radical.

Despite the fact that the high iron(III) extraction degree by the mixture was achieved at the 50–60 vol.% (E = 98.4%) concentration of 2-undecanone, for further iron(III) extraction from the bauxite leaching solution, a mixture of 70 vol.% C_8 + C_{10} and 30 vol.%

2-undecanone (E = 95.9%) was used. Aliphatic alcohols are the cheapest reagent; this makes the application of this mixture in an industry more promising.

3.1.2. Effect of Dilution of Extractants on Iron(III) Extraction

The effect of the extractant concentration on iron(III) extraction was investigated. It was found that dilution had the greatest effect on the extraction ability. Extraction degree was 2.5% for 20 vol.% 2-undecanone, 25% for 20 vol.% $C_8 + C_{10}$, 27.5% for the 20 vol.% mixture $C_8 + C_{10}$ (70 vol.%), and 2-undecanone (30 vol.%) in dodecane (Figure 5). With an increase in the extractant concentration, the iron(III) extraction degree significantly increased. At the 80 vol.% of extractant concentration, E was 75.1%, 83.4%, and 91.7% for alcohol, ketone, and their mixture. The significant difference between the extraction with diluted 2-undecanone and $C_8 + C_{10}$ can be explained by the similar effect of an inert diluent on alcohol observed upon dilution with a ketone (see Section 3.1.1). Aliphatic alcohols in a concentrated solution exist primarily in the associated molecules [38]. When diluted with an inert diluent, as with diluting with a ketone, the excess enthalpy increased [39]. Although the enthalpy was lower when diluted with an inert diluent than when diluted with a ketone, the hydroxyl bond in the alcohol associates was weakened similarly. The result was the destruction of associates and the formation of more active monomers. Ketones do not self-associate through hydrogen bonds due to the absence of a proton donor group in the molecule [38], therefore, at dilution, the ketone concentration and, consequently, its extraction ability, decreases.
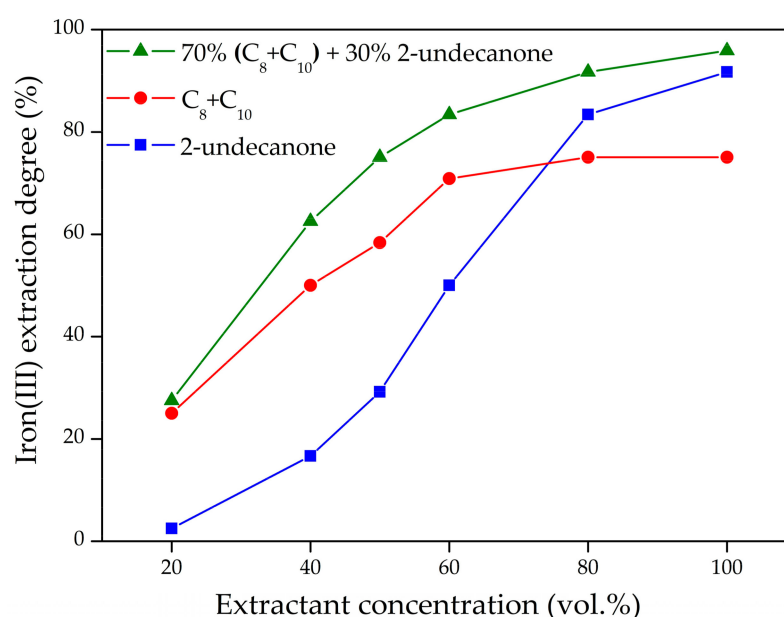

Figure 5. Effect of extractant concentration on iron(III) extraction at C(HCl) = 5.7 M, C(Fe) = 8.4 g/L, O:A = 1:1.

Iron(III) was extracted with a mixture of ketone and alcohol better over the entire range of the studied concentration of extractants. In dilute solutions, extraction increased due to the formation of monomeric alcohol molecules, while in concentrated solutions, it was due to the presence of a ketone in the mixture.

Based on the dependence for the iron(III) distribution coefficient on the concentration of the extractant (Figure 6), it can be concluded that for the extraction of 1 mol of iron(III), it requires ~4 mol of 2-undecanone, 1.5 mol of $C_8 + C_{10}$, and 2.5 mol of a mixture of alcohol with the ketone. The extraction of 1 mol of iron(III) requires about 3 mol of MIBK [40]. At high HCl concentrations, iron(III) is extracted by neutral oxygen-containing extractants and

their mixtures in the $HFeCl_4$ form [24,41]. The solvent extraction process can be written by the following equations:
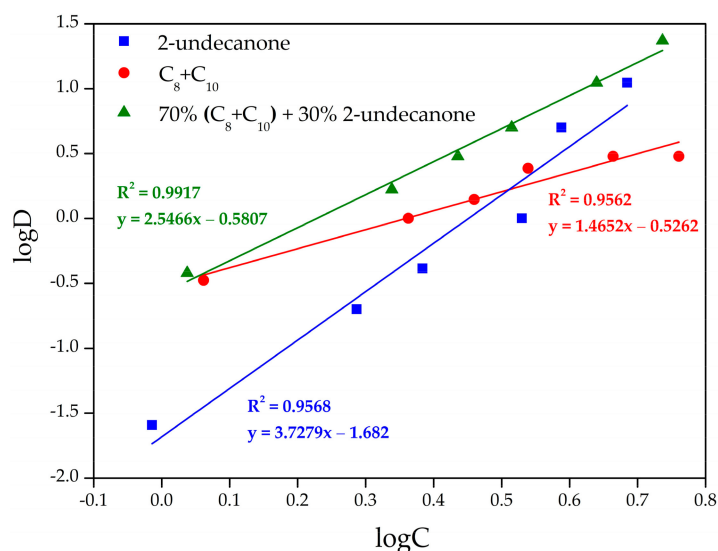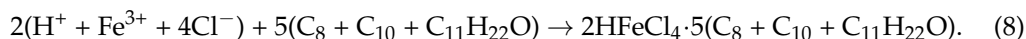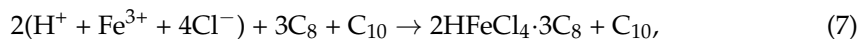
$$H^+ + Fe^{3+} + 4Cl^- + 4C_{11}H_{22}O \rightarrow HFeCl_4 \cdot 4C_{11}H_{22}O, \tag{6}$$

$$2(H^+ + Fe^{3+} + 4Cl^-) + 3C_8 + C_{10} \rightarrow 2HFeCl_4 \cdot 3C_8 + C_{10}, \tag{7}$$

$$2(H^+ + Fe^{3+} + 4Cl^-) + 5(C_8 + C_{10} + C_{11}H_{22}O) \rightarrow 2HFeCl_4 \cdot 5(C_8 + C_{10} + C_{11}H_{22}O). \tag{8}$$

Figure 6. Log–log relation between the distribution coefficient Fe(III) and extractant concentration at C(HCl) = 5.7 M, C(Fe) = 8.4 g/L, O:A = 1:1.

3.2. Iron(III) Extraction from Al Chloride Solution of Bauxite HCl Leaching by Mixture of $C_8 + C_{10}$ Alcohols and 2-Undecanone

3.2.1. Iron(III) Extraction by a Mixture of Alcohols $C_8 + C_{10}$ (70 vol.%) and 2-Undecanone (30 vol.%)

A comparison of the extraction capacity of oxygen-containing extractants for iron(III) extraction from the Al–Cl solution after bauxite leaching at O:A = 1:3 was studied (Figure 7). It was found that iron(III) was fully extracted by 2-octanone and its mixture with 1-octanol at a ratio of 1:1. 2-octanone has a low flash point (Table 1), this type of extractant is a flammable liquid. Due to this fact, it is difficult to use 2-octanone in industry. The iron(III) extraction degree by the synergistic mixture $C_8 + C_{10}$ (70%) + 2-undecanone (30%) was comparable to the extraction by pure 2-nonanone. The iron(III) extraction degree using pure 2-undecanone was less than 50%. Therefore, the synergistic mixture was used for further study.

To study the extraction of iron(III) from a HCl solution with a mixture of $C_8 + C_{10}$ (70 vol.%) and 2-undecanone (30 vol.%), a McCabe–Thiele plot was obtained (Figure 8). It was found that using a solution of the composition, g/L: Fe-7.47, Al-1.7, Ca-0.35, Cr-0.35, and 6 M HCl, it is possible to completely extract iron(III) from the aqueous phase at a O:A ratio = 1:2 for two steps and O:A = 1:4 for three steps. At a lower O:A ratio, an almost quantitative extraction of iron(III) occurred for 1–2 steps, but this led to obtaining an organic phase with a lower iron(III) concentration. This makes it difficult to obtain a concentrated $FeCl_3$ solution at the stripping stage. The obtained raffinate can be returned to the bauxite leaching stage.
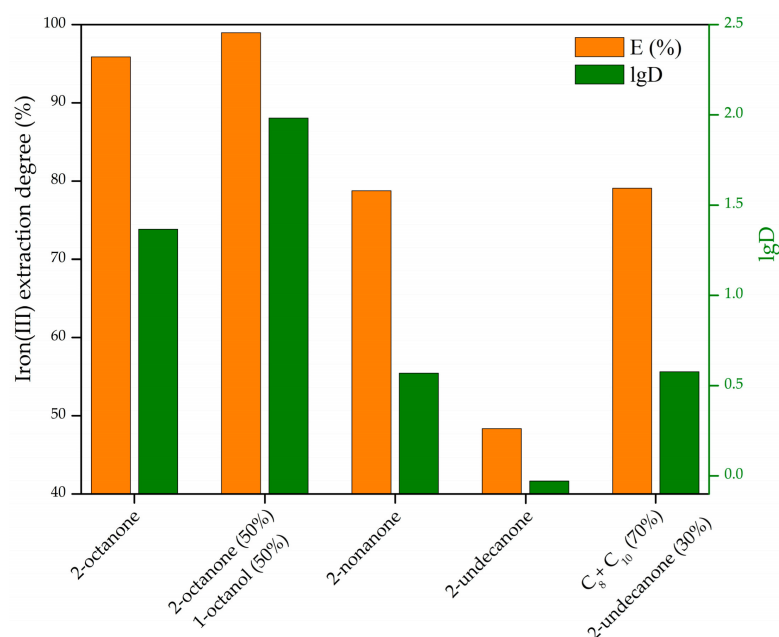
Figure 7. The dependence of iron(III) extraction degree (E) and distribution ratio (D) on the oxygen-containing extractant from bauxite leaching solution at C(HCl) = 6 M, C(Fe) = 9.7 g/L, O:A = 1:3.

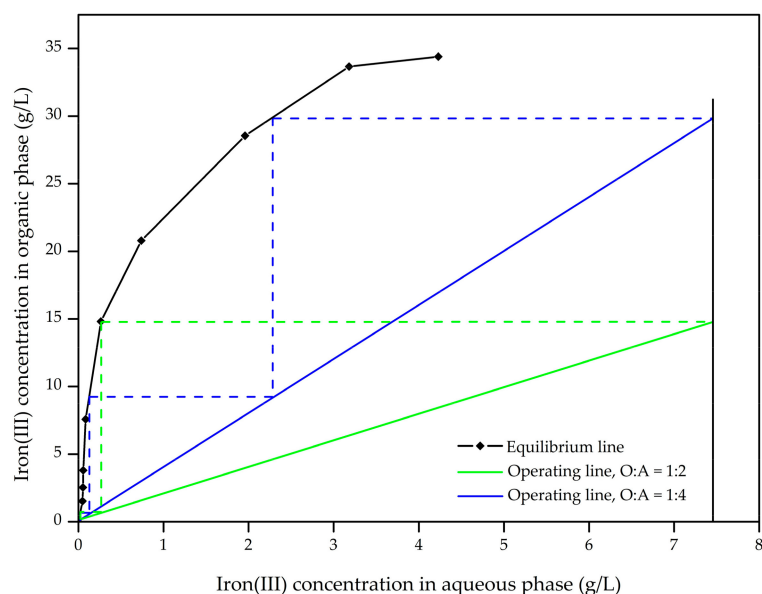**Figure 8.** McCabe–Thiele plot for iron(III) extraction at different O:A ratios at C(Fe) = 7.47 g/L, C(HCl) = 6 M.

3.2.2. Scrubbing of Organic Phase from Non-Ferrous Metals

The aluminum (Al), calcium (Ca), and chromium(III) (Cr) were dissolved during bauxite HCl leaching and co-extracted with iron(III) from the solution (Figure 9). To obtain an iron(III) extract purified from impurities, the scrubbing of the organic phase at different O:A ratios was studied (Figure 10). To avoid iron(III) stripping to scrub the solution with impurities, 7 M HCl was used as the scrubbing solution. The 7 M HCl does not strip iron(III) because an oxygen-containing reagent extracts iron from a high concentration hydrochloric acid solution (here 6 M). Extraction proceeds because of the formation of a chloride complex (Section 3.1.2) that cannot be destroyed by a concentrated HCl solution. This means that the stripping of iron(III) will be minimal when the organic phase is scrubbed by more concentrated hydrochloric acid. As can be seen from Figure 9, the scrubbing degree from

impurities was maximum at a O:A ratio = 5:1 and reached Al-64.7%, Ca-72.3%, and Cr(III)-60.2% through one step. In this case, about 1.3% of iron(III) passed into the scrub solution. It was necessary to carry out two stages of scrubbing at a O:A ratio = 5:1 to obtain a pure iron(III) extract.
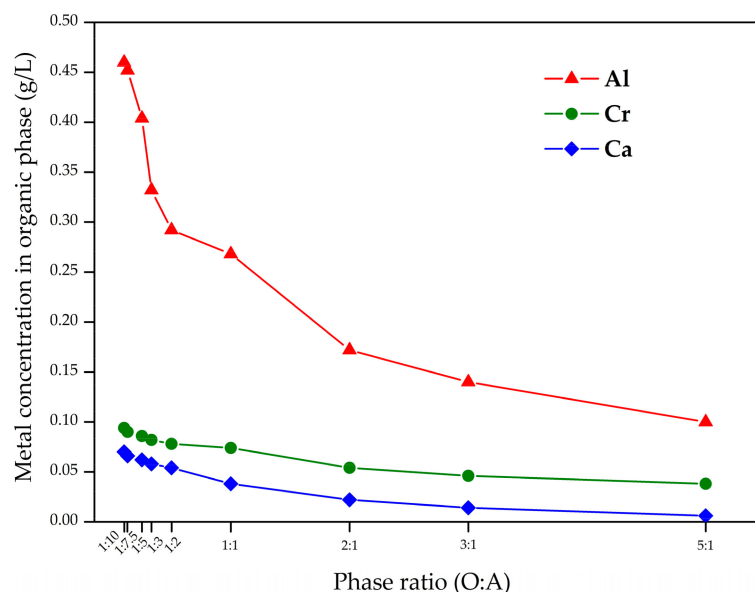

Figure 9. Al, Ca, and Cr(III) co-extraction with iron(III) at different O:A ratios at C(Al) = 2.7 g/L, C(Ca) = 0.35 g/L, C(Cr(III)) = 0.35 g/L, and C(HCl) = 6 M.

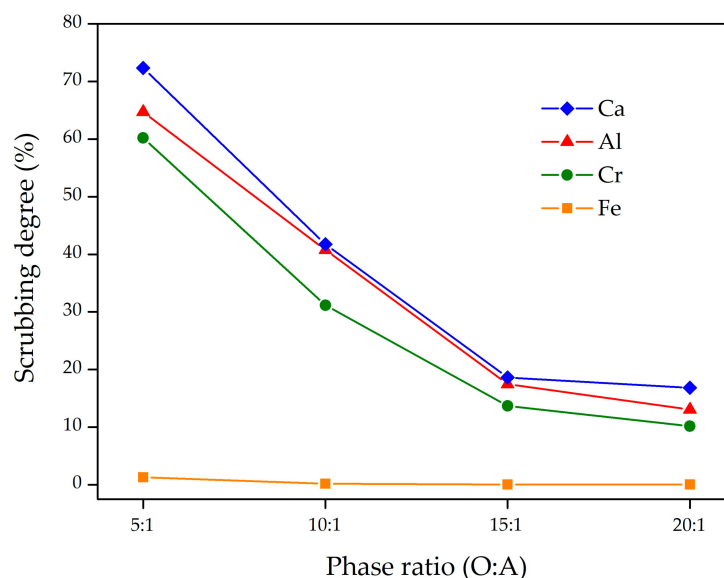**Figure 10.** Scrubbing of the iron(III) extract from Al, Ca, and Cr(III) at different O:A ratios by 7 M HCl at C(Fe)org. = 14.68 g/L, C(Al)org. = 0.35 g/L, C(Ca)org. = 0.04 g/L, and C(Cr(III))org. = 0.06 g/L.

3.2.3. Iron(III) Stripping

To study the iron(III) stripping from a mixture of C_8 + C_{10} (70%) + 2-undecanone (30%), a stripping McCabe–Thiele plot was plotted at various concentrations of iron(III) in the organic phase (Figure 11). A solution of 0.2 M HCl was used as a stripping agent to avoid the formation of a third phase. In aqueous and low-concentration HCl solutions, iron(III) is predominantly in the form of Fe^{3+}, $FeCl^{2+}$, and $FeCl_2^+$ [42]. Upon contact of the organic phase saturated iron with them, the $HFeCl_4$ complex is destroyed, due to which iron(III) passes into the aqueous phase. At a concentration of iron(III) in the organic phase

of 20 g/L, it can be removed by one step of stripping. Iron(III) concentration in this case was 0.42 g/L at O:A = 1:1. Using two steps of stripping, iron(III) could be removed to a concentration of 0.12 g/L at the O:A = 2:1. This fact indicates the possibility of obtaining a strip solution concentrated for iron.
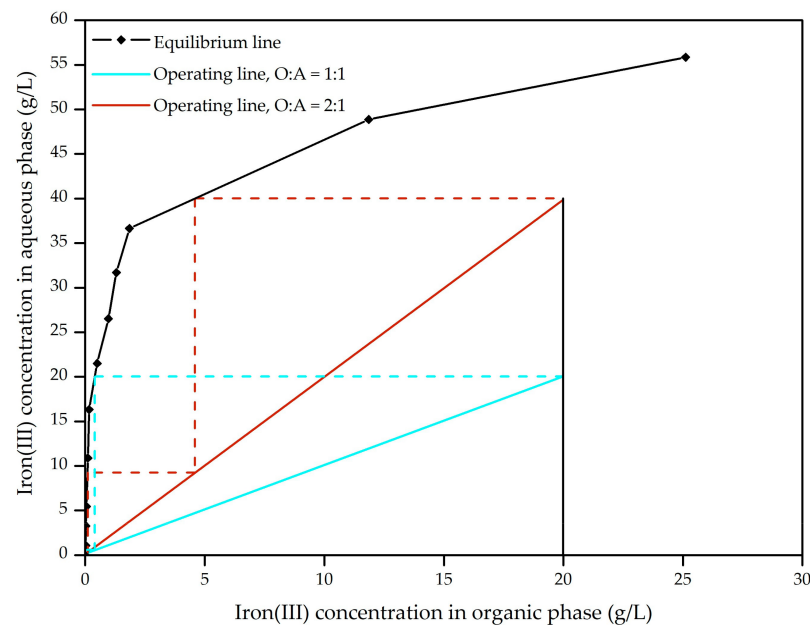

Figure 11. McCabe–Thiele plot for iron(III) stripping at different concentrations in the organic phase at O:A = 1:1, C(HCl)aq. = 0.2 M.

3.2.4. Iron(III) Extraction at the Cascade of Extractors Mixer-Settler Types by the Mixture of Alcohols $C_8 + C_{10}$ and 2-Undecanone

The aim of the tests carried out on a counter-current cascade of mixing-settling extractors was to remove the main part of Fe(III) from the chloride leaching solution of bauxite to obtain a pure and concentrated solution of ferric chloride. The laboratory continuous extraction cascade consisted of nine chambers: three extraction chambers, two scrabbing chambers, and four stripping chambers. The scrub solution was added to the extraction step. The ratio of the organic and aqueous phases during the extraction was maintained at the level of O:A = 1:2.5, and during the scrubbing and the stripping, O:A = 5:1. The initial solution was a solution of hydrochloric acid leaching of bauxite with the composition, g/L: Fe-10.17, Al-2.36, Ca-0.43, Cr-0.24, and 6 M HCl. 7 M HCl was used as a scrubbing solution, and 0.2 M HCl was used as a stripping agent. The scheme of the extraction cascade is shown in Figure 12, and the aqueous phases corresponding to the chamber are shown in Figure 13.
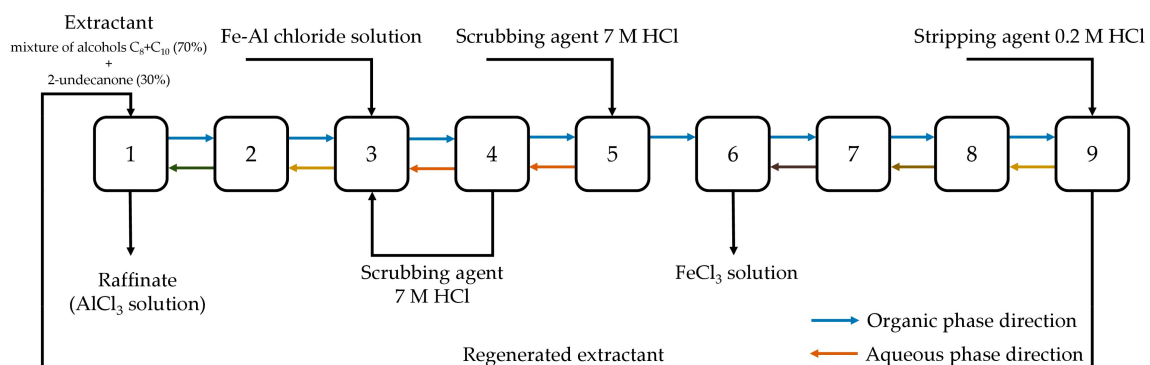

Figure 12. Scheme of the 9-stage extraction cascade for iron(III) extraction.

Figure 13. Aqueous phase from the corresponding chamber of the cascade.

The compositions of the solutions obtained on the extraction cascade in the course of continuous operation are shown in Table 3. It can be seen that the iron(III) content in the initial chloride solution could be reduced by the solvent extraction to 0.84 g/L, which corresponded to E(Fe) = 91.7%. The iron(III) extraction degree can be increased by decreasing the O:A ratio at the extraction stage. However, this will lead to a decreased iron(III) concentration in the organic phase and, consequently, in the strip solution. There is no need for full removal of iron(III) from the aqueous phase since after extraction, the raffinate is sent for the re-leaching of bauxite. As a result of solvent extraction, a $FeCl_3$ solution containing 90.5 g/L of iron(III) was obtained. This solution can be treated by the pyrohydrolysis method to obtain the pigment iron oxide and to regenerate HCl [43].

Table 3. Composition of the feed solution, raffinate, scrubbing solution, and $FeCl_3$ solution.

Solution	Metal Concentration, g/L			
	Fe	**Al**	**Ca**	**Cr**
Feed	10.17	2.36	0.43	0.31
Raffinate	0.84	2.35	0.41	0.30
Scrub solution	4.99	0.034	0.026	0.018
$FeCl_3$ strip solution	90.50	0.007	0.023	0.007

Based on the obtained results, a schematic flowsheet of the solvent extraction of iron(III) from chloride solution after HCl leaching of bauxite is shown in Figure 14. This includes obtaining the iron(III) oxide from pure $FeCl_3$ solution by pyrohydrolysis and recycling the HCl for further use in the iron removal process [44,45].
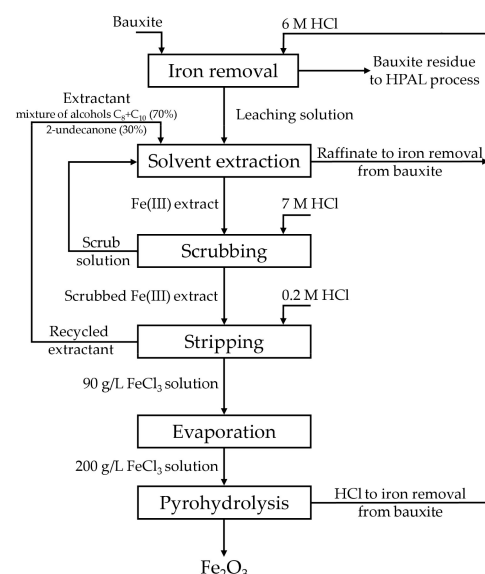

Figure 14. Schematic flowsheet of iron(III) removal from the chloride solution after bauxite HCl leaching.

4. Conclusions

In this research, the solvent extraction of iron(III) from a chloride solution of bauxite HCl leaching by neutral oxygen-containing extractants and their mixtures was studied.

The presence of a synergistic effect using a mixture of $C_8 + C_{10}$ and 2-undecanone was found. The maximum synergistic effect was observed at the ketone concentration of 50–60 vol.%. The solvation numbers of iron(III) extraction by a mixture of alcohols 1-octanol and 1-decanol, 2-undecanone and their mixture containing 70 vol.% $C_8 + C_{10}$ and 30 vol.% ketone were determined.

The iron(III) extraction from chloride solution was possible at the O:A ratio = 1:2-4 in 2-3 steps with an initial iron(III) concentration for 7.4 g/L by a mixture of $C_8 + C_{10}$ (70%) + 2-undecanone (30%).

The scrubbing of the extract by 7 M HCl at an O:A ratio = 5:1 removed up to 64.7%, 72.3%, and 60.2% the Al, Ca, and Cr(III), respectively. The iron(III) losses into the scrubbing solution did not exceed 1.3%. It is possible to concentrate iron(III) by stripping and obtaining a $FeCl_3$ solution.

During extraction on a counter-current cascade of mixing-settling type extractors a $FeCl_3$ solution, g/L: Fe-90.5, Al-0.007, Ca-0.023, Cr-0.007, and raffinate, g/L: Al-2.35, Fe-0.86, Ca-0.43, Cr-0.31 were obtained. A schematic diagram of the iron(III) solvent extraction process was proposed, which includes sending raffinate for the re-leaching of bauxite as well as obtaining iron(III) oxide from the strip solution.

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