Removal of Iron (III) from Ammonium Alum Solution of Coal Fly Ash H_2SO_4 + NH_4HSO_4 Leaching by Ion Exchange Sorption Using Purolite S957 and S950 Resins

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Abstract

In this research, the ammonium alum solution was purification from Fe (III) – the main impurity in the acid technology for alumina production using ion exchange method. The acid solution was obtained after Coal Fly Ash high-pressure leaching by 7.5M H_2SO_4 + 40% NH_4HSO_4 mixture at T = 210 ºC. Two type of resins, Purolite S957 and S950 were used in sorption tests. At optimum parameters (T = 25 ºC, sorption time 24 h and the resin to solution ratio - 1:25), it is possible to extract more than 90% of iron. Using the Langmuir model, the batch sorption values for iron were calculated: for Purolite S957 resin - 19.48 g/g; for Purolite S950 - 3.39 g/g. The dynamic sorption was studied for Purolite S957 resin at a solution flow rate of 0.4, 0.65, and 1.6 specific volumes ($V_{sp.vol.}$) per min. Using the Thomas model, dynamic capacity values were calculated for each of the rates: 0.4 $V_{sp.vol.}$/min - 6344.56 mg/g; 0.65 $V_{sp.vol.}$/min - 5590.23 mg/g; 1.65 $V_{sp.vol.}$/min - 1632.77 mg/g. The desorption of Fe(III) from resin using 2M H_2SO_4 at the rate of 0.4-0.65 $V_{sp.vol}$ was studied. The required volume of desorbent at both rates is 6 $V_{sp.vol.}$. The possibility of removal the Fe(III) from ammonium alum solution by 12 times (from 27.2 mg/L to 2.2 mg/L) using Purolite S957 resin was founded.

Keywords: Coal fly ash, High pressure leaching, Ammonium bisulfate, Resin sorption, Iron removal.

1. Introduction

Currently, one of the main areas of utilization of solid waste from coal-fired thermal power plants, coal fly ash – CFA, is the extraction of non-ferrous metals. CFA is a promising raw material for alumina production due to the high content of aluminum oxide, from 20 to 40 wt. %, the absence of the need to grind the raw material and the low cost (basically, the cost of CFA includes only the cost of delivery to the consumer). Reftinskaya GRES the largest coal power plant in Russia, generates more than 4 Mt of CFA per year, and the total CFA store in the landfills exceeds 180 Mt. This CFA can be used at Russian alumina refineries in the Urals region, since Reftinskaya GRES is located 120 km and 490 km from the Urals and Bogoslovsky aluminum plants, respectively [1].

It is not effective to use alkaline methods (Bayer and sintering) to extract alumina from this type of CFA, due to the low content of aluminum oxide (25-28 wt. %) compared to CFA from the Inner Mongolia of China (40-45 wt. %) [2]; thus, resulting in high consumption of fluxes during the preliminary high-temperature treatment and alkali during the leaching process. For the CFA of the Reftinskaya GRES, it is efficient to use acid methods. Previously, it was shown that the hydrochloric acid method can be used to extract alumina [3]. An alternative is the bisulfate method, which allows the use of less aggressive reagents for CFA leaching – a mixture of ammonium bisulfate and sulfuric acid [4,5].

The main impurity in acid methods is iron, which, together with aluminum, is almost completely extracted into solution during the leaching process. Previously, a solvent extraction method for iron removing from Al-Cl liquor was studied to obtain of ferric chloride solution [6]. Another approach would be to use iron selective ion exchange resins. In this study, the purification of ammonium alum solution obtained after leaching of the CFA using Purolite S957 and S950 resins was investigated.

2. Materials and Methods

2.1 Materials and Reagents

CFA was collected from the Reftinskaya GRES (Asbest, Russia). Ammonium sulfate CAS No. 7783-20-2, sulfuric acid CAS No. 7664-93-9 (both from SigmaTek, Russia) were used in the present study. Distilled water was used to washing and dilute of ammonium alum after CFA leaching and liquor cooling. The ion exchange resins S957 and S950 (Purolite, USA) were used for sorption research.

2.2 Experiments

The CFA was leached with a mixture of 40% ammonium bisulfate and 7.5M sulfuric acid at 210 °C, S:L = 1:10, with a duration of 180 min. After slurry filtration, the solution was cooled to room temperature and ammonium alum crystals ($NH_4Al(SO_4)_2 \cdot 12H_2O$) was precipitated. These crystals were washed with cold distilled water (3 ºC), since at this temperature the solubility of ammonium alum is minimal: 5 g / 100 ml of H_2O. The loss of alum after washing was 14%. Next, the crystals were dissolved in distilled water for iron removal study.

Resins were placed in 2M sulfuric acid for 3 h to converted it into the H^+ form. Fe batch sorption experiments were performed by mixing a certain amount of Purolite S957 and S950 with an ammonium alum solution of a known concentration in a plastic Erlenmeyer flask. The Erlenmeyer flasks were agitated at 100 rpm with an ECROS PE-6300 laboratory shaker (LLC ECROSKHIM, Russia) at temperatures of 25, 40 and 55 ºC until pseudo-equilibrium was reached. For dynamic sorption, a column filled with resin was used; the solution was fed into the column using a peristaltic pump YW21-SP25 (YW FLUID, China).

2.3 Analytical Methods

The metals concentrations in liquor after CFA leaching and resin sorption were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) using an atomic absorption spectrometer AA-240FS (Varian, Melbourne, Australia).

3. Results and Discussion

3.1 Batch Sorption

Before carrying out experiments on batch sorption, the impurity composition of the solution after CFA leaching, water washing of precipitated ammonium alum and alum solution were analyzed (Table 1).

Table 1. The impurities concentration in the liquor after CFA leaching, ammonium alum washing water and alum solution (mg/L).

Sample	Al	Ca	Cr	Fe	K	Mg	Mn	Na	P	Si	Ti
Liquor	778	153	11.6	1460	60.3	252	33.7	154	126	19.3	157
Ammonium alum washing water	2150	190	3.8	88	5.2	14.7	1.7	12.6	6.5	0.51	8.1
Alum solution	3720	249	4.3	27.2	1	0.51	0.04	1	0.5	0.006	0.53

Most of the Fe remains in the liquor after crystal precipitation, where Fe concentration is 1.4 g/L, after washing the alum by cold water, the iron content in the alum solution is 27.2 mg/L. For Fe batch sorption the Purolite resin was used, as during the literature review information of the high selectivity of two types of resin S957 and S950 to iron(III) was found in acid solutions [7,8]. The main characteristics of the resins are presented in Table 2.

Table 2. The chemical and physical characteristics of Purolite resin [9].

Properties and characteristics	S957	S950
Polymer structure	Macroporous crosslinked polymer	
Form	Spherical beads	
Functional group	Phosphonic and sulfonic acid	Aminophosphonic
Ionic form	H^+	Na^+
Mean Size Typical	315 – 850 µm	300 – 1200 µm
Specific Gravity	1.12 g/mL	1.13 g/mL
Shipping weight (approx.)	710 – 760 g/L	710 – 760 g/L

At the first stage of the research, the effect of pH solution on the sorption of four elements (Al, Fe, Ca, and Ti) was determined. Sorption was carried out at T = 25 ºC τ = 240 min. Figure 1 shows the dependencies on the effect of the pH of the ammonium aluminum alum solution on the extraction of the main elements.

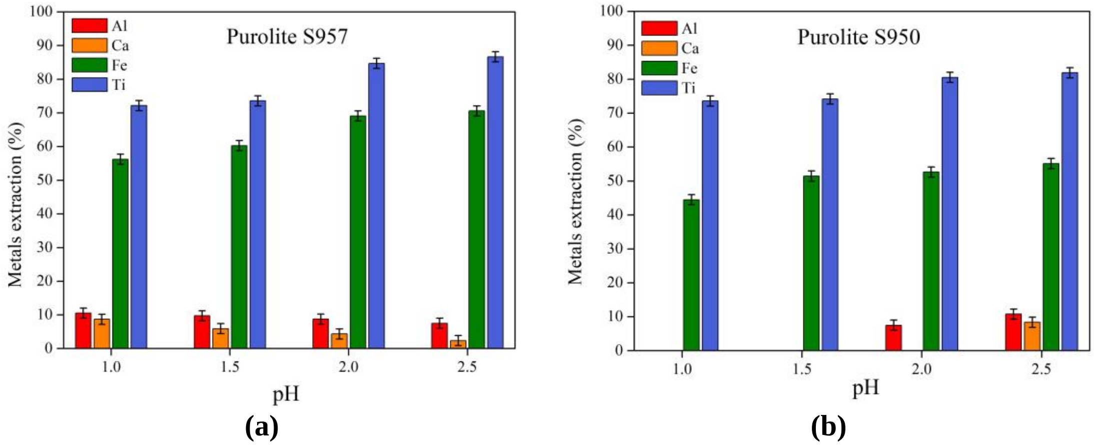
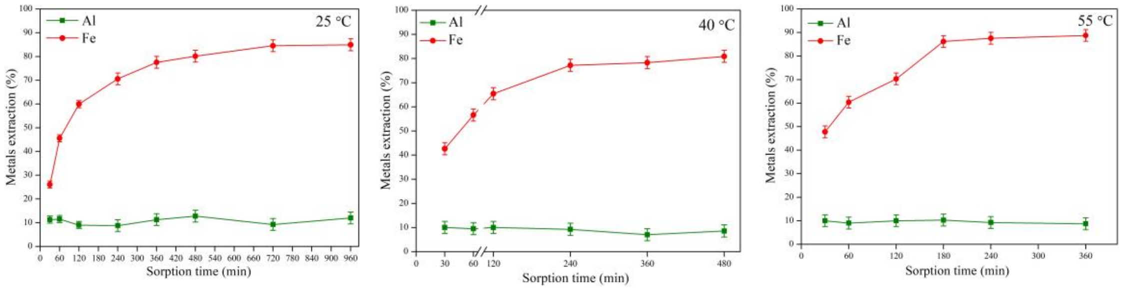


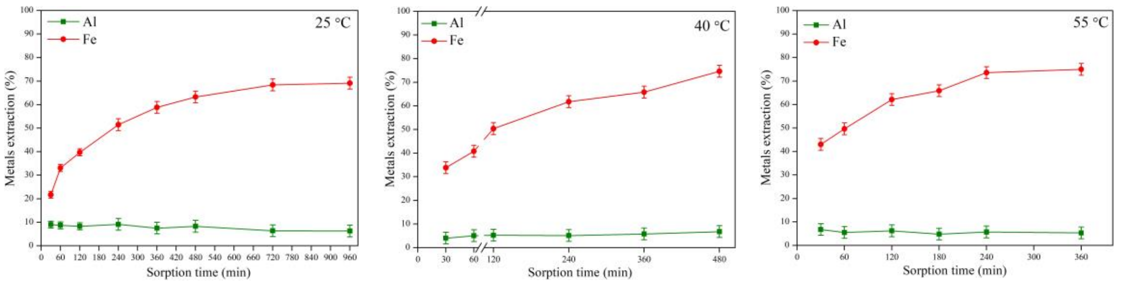
Figure 1. The effect of the pH of alum solution for the metal's extraction (S/L ratio = 1:100): (a) for Purolite S957 resin; (b) for Purolite S950 resin.

As can be seen from Figure 1, pH has a significant effect on metals extraction. For the S957 resin, the Fe extraction at pH = 1 is 56%, at pH = 2.5 it increases to 70% (Figure 1a). The S950 resin is more selective for iron (max extraction is 55% at pH = 2.5), since at pH = 1.5 Ca and Al do not transfer into the resin and therefore do not reduce its capacity, Al is not lost (Figure 1b). Thus, subsequent experiments to study the effect of temperature and amount of resin (S/L ratio) were carried out at pH = 2.5 for S957 and pH = 1.5 for S950 (Figures 2-3).



(a) (b) (c)

Figure 2. Effect of solution temperature on Fe extraction by Purolite S957 resin (S/L ratio = 1:100): (a) T = 25°C; (b) T = 40 °C; (c)T = 55 °C.



(a) (b) (c)

Figure 3. Effect of solution temperature on Fe extraction by Purolite S950 resin (S/L ratio = 1:100): (a) T = 25°C; (b) T = 40 °C; (c)T = 55 °C.

As can be seen at room temperature, after 720 min of sorption, the Fe extraction remained practically unchanged for both resins: 85% for S957 (Figure 2a) and 70% for S950 (Figure 3a). Increasing the temperature to 40 °C reduced the sorption time to 480 min for S957 resin (Figure 2b). Using Purolite S950, there was a slight increase in the Fe extraction, up to 75% at 480 min of sorption (Figure 3b). When the solution temperature was 55 °C, there was a slight increase of Fe extraction to 89% for S957 resin at 240 min of sorption (Figure 2c). For S950 resin, the max Fe extraction was 75% at the same sorption time (Figure 3c). The study of the effect of the S/L ratio (amount of resin to the solution) was carried out in the range of 1:25 to 1:1000 at T = 25 °C and the sorption time 24 h (Figure 4).

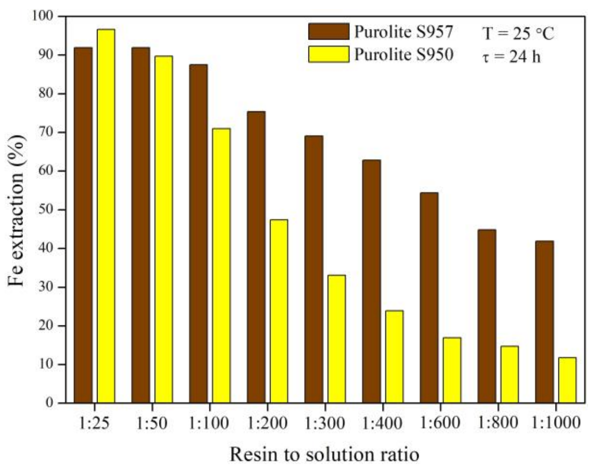


Figure 4. Effect of resin to solution ratio on Fe extraction.

As can be seen from the Figure 4, at high values of S:L = 1:300-1000, the Fe extraction for S950 resin did not exceed 35%, while for S957 this value was 70%. However, as the amount of resin was increased to the S:L ratio = 1:25, the Fe extraction efficiency for S950 was already 96%, while for S957 it remained at 92%. This phenomenon may be due to S957 having the ability to extract more Al than S950, thereby reducing the resin capacity and did not allow extracting the max of Fe.

To further determine the batch sorption capacity of resins, based on the experimental data (Figure 4), isotherms were calculated and described using the Freundlich and Langmuir models [10] as shown in Equations 1 and 2. The obtained dependencies are shown in Figure 5.

The Freundlich model:

$$Q_e = K_f \times C_e^n \tag{1}$$

where Q_e is the value of equilibrium sorption, mg/g; C_e is the equilibrium concentration of the sorbate in the solution, mg/L; K_f is the Freundlich constant, dm^3/g; n is an empirical parameter. This model assumes the presence many layers through which diffusion of sorbed metal ions occurs.

The Langmuir model:

$$Q_e = (Q_m K_L C_e)/(1 + K_L C_e) \tag{2}$$

where Q_m is the value of maximum sorption, mg/g; C_e is the equilibrium concentration of the sorbate in the solution, mg/L; K_L is the Langmuir constant, dm^3/mg. This model describes sorption on the resin surface through a monolayer.

The capacity of the resins was determined through the values of the Fe concentration in solutions using Equation 3:

$$Q_{eFe} = (C_i - C_f C_e) \times V/m \tag{3}$$

where Q_{eFe} is the capacity of the resin, mg/g; C_i and C_f are the initial and final Fe concentrations in the solution, mg/L, V is the volume of the solution, L and m is the mass of resin, g.

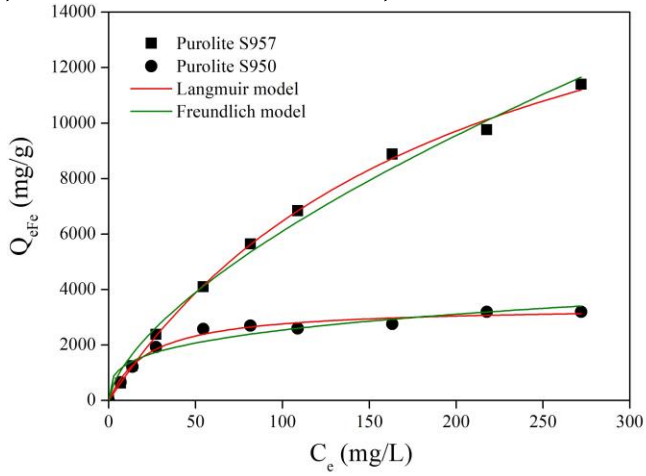


Figure 5. Sorption isotherms for Purolite S957 and Purolite S950 resins.

Correlation coefficient data (Table 3) show that the Langmuir model is the most suitable for describing Fe sorption process, which indicates a monolayer sorption mechanism. According to Table 3, the max theoretical Langmuir resin capacity for Fe is 19.48 g/g for S957 resin and 3.39 g/g for S950. Based on these data, S957 resin was chosen for further experiments on sorption in dynamic mode, since its batch capacity is more than 5.5 times higher when compared to S950**.**

Table 3 Calculation of correlation coefficients for sorption models.

Model	**Parameters**	**S957**	**S950**
Langmuir	Q_m, mg/g	19481.98	3390.09
	K_l, dm^3/mg	0.00497	0.04393
	R^2	0.998	0.982
Freundlich	n	1.546	3.413
	K_f, dm^3/g	310.67	658.91
	R^2	0.991	0.928

3.2 Dynamic Sorption

For the experiments on dynamic sorption, three speeds of 0.4, 0.65 and 1.6 specific volumes ($V_{sp.vol.}$) per min were chosen. Sorption was carried out until complete Fe breakthrough. The analysis of the obtained experimental data was carried out using the Thomas model (Figure 6). This model assumes that the process follows Langmuir adsorption-desorption kinetics without axial dispersion. The Thomas model is as shown in Equation 4:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\frac{K_{Th}}{Q}(q_{0M}M - C_0V)\right)} \tag{4}$$

where K_{Th} is the Thomas rate constant, mL/min·mg; q_0 is the equilibrium capacity of the adsorbent (mg/g); *M* is the weight of the column loading, g; *Q* is the volumetric flow rate (mL/min); *V* is the volume of the solution passed through the column, mL.

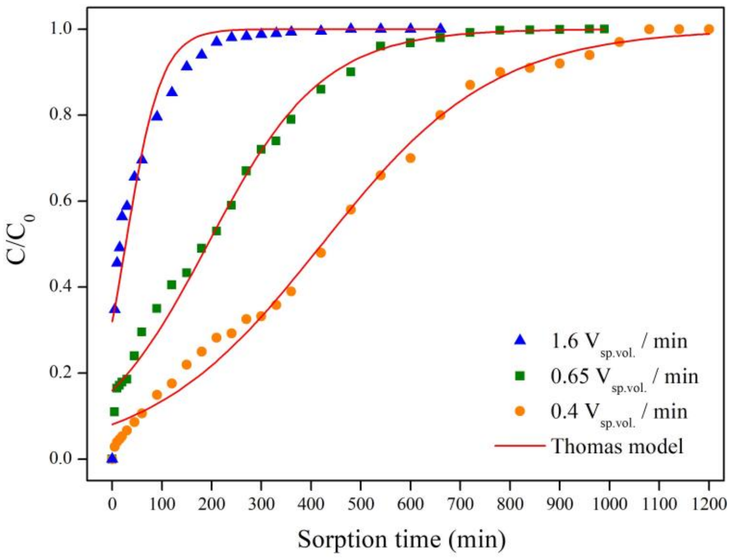


Figure 6. Experimental tests of the dynamic sorption Fe extraction from aluminum alum solutions by Purolite S957.

From Figure 6, the saturation of the resin at a solution flow rate of 0.4 $V_{sp.vol.}$/min occurs in 1100 min, at 0.65 $V_{sp.vol.}$/min in 800 min, and at 1.6 $V_{sp.vol.}$/min in 400 min respectively. After analyzing the experimental results using the Thomas model, high values of the correlation coefficient (R^2) were obtained. This fact indicates the applicability of this model to describe the process of iron sorption using S957 resin (Table 4). The value of the Thomas rate constant with an increase in the rate of passage of the solution from 0.4 to 1.6 $V_{sp.vol.}$/min increased by 4.8 times, but the value of dynamic capacity decreased from 6344.56 mg/g to 1632.77 mg/g. These values were significantly lower than the capacity of batch sorption (Table 3).

Table 4. Thomas model constants, resin capacities and correlation coefficients obtained from experimental data (Figure 6) of the Fe extraction by dynamic sorption from aluminum alum solution using Purolite S957.

Solution flow rate, $V_{sp.vol.}$/min	K_{Th}, mL/min·mg	q_0, mg/g	R^2
0.4	1.92×10^{-4}	6344.56	0.992
0.65	2.97×10^{-4}	5590.23	0.987
1.65	9.23×10^{-4}	1632.77	0.904

According to the literature review [9], Fe was desorbed with a 2M H_2SO_4 solution (Figure 7). As can be seen, regardless of the desorbent feed rate (0.4 or 0.65 $V_{sp.vol.}$/min), almost full Fe removal from the resin occurs using 6 $V_{sp.vol.}$ of desorbent.

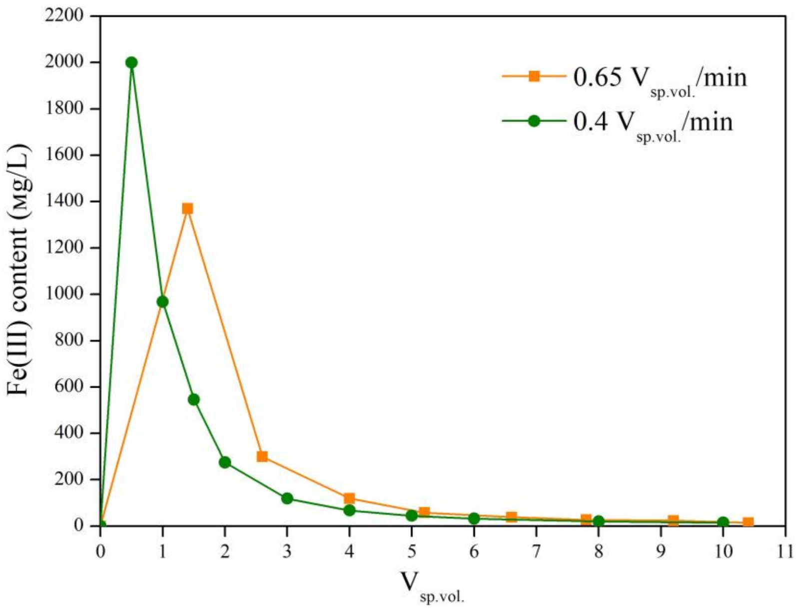


Figure 7. The desorption of Fe from the Purolite S957 depending on the 2M H_2SO_4 feed rate.

4. Conclusions

The Fe extraction from ammonium alum solutions after CFA leaching by the method of ion exchange sorption was investigated. The use of Purolite S957 can be used to reduce the Fe content in solution by 12 times (from 27.2 mg/L to 2.2 mg/L).

Acknowledgements

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5. References

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