Boehmite-Kaolinite Bauxite Treatment by Ammonium Bisulfate Method: Study of $Al(OH)_3$ Precipitation from Ammonium Alum Solution

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Abstract

The precipitation of aluminum hydroxide ($Al(OH)_3$) from ammonium alum solution by ammonia water was studied. Ammonium alum solution was obtained after high-pressure leaching of boehmite-kaolinite bauxite with a mixture of 3M H_2SO_4 + 40% NH_4HSO_4 at T = 170 ºC. Fe(III) was extracted from the ammonium alum solution by ion-exchange sorption using Purolite S957 resin. Analyze the precipitation experiments, the influence of seed addition to shape of particle, the phase composition, the content of impurities, and the size of the $Al(OH)_3$ particles were investigated. The $Al(OH)_3$ calcination process at T = 900 ºC to obtain alumina powder was studied.

Keywords: Bauxite, High-pressure leaching, Ammonium bisulfate method, $Al(OH)_3$ precipitation, Sand grade alumina.

1. Introduction

Currently, two deposits located in the Urals are used in Russia for alumina production – North Urals and Middle Timan. The bauxite of these deposits has a low silica (SiO_2) content – 3-5 wt.%, therefore, alkali methods (Bayer and sintering) are used for its treatment [1]. However, the total amount of sandy grade alumina that produced in Russia is not enough to compare to the requirements of Aluminum Smelters. Therefore, it is necessary to look for new sources of alumina. In the Arkhangelsk region, there is an explored bauxite of Severoonezhsk deposit. Annually about 900 kt are mined, this bauxite is not used to produce alumina, due to the high content of silica (up to 20 wt. %) and chromium oxide Cr_2O_3 (up to 1 wt. %) [2].

The most promising methods for obtaining alumina from such raw materials are acidic, which allow the extraction of almost all aluminum, while silica remains in the solid residue [3]. Previously, the leaching process of bauxite with a mixture of sulfuric acid and ammonium bisulfate was studied [4]. In this article, the process for alumina production from acid liquor was studied and the behavior of the main impurities was analyzed.

2. Materials and Methods

2.1 Materials and Reagents

Raw bauxite sample was collected from the Severoonezhsk Bauxite Mine (N62.573349º, E39.719039º). Analytical grade ammonium sulfate CAS No. 7783-20-2, sulfuric acid CAS No. 7664-93-9 (both from SigmaTek, Russia) were used in the bauxite leaching process. Distilled water was used to washing bauxite, washing and dilute of ammonium alum after bauxite leaching and liqour cooling. The ion exchange resins S957 (Purolite, USA) were used for Fe removal from

alum solution by resin sorption method. The gibbsite powder ($Al(OH)_3$) from Urals Alumina refinery was used as seed in the precipitation process.

2.2 Experiments

Bauxite was leached by 40% NH_4HSO_4 + 3M H_2SO_4 mixture in a 50 mL high-pressure reactor (Deschem, China). The leaching time at T = 170 ºC was 90 min. The liquid to solid ratio (L:S) was 10. Pulp after leaching was filtered, the solid residue was washed by heat water (90 ºC). The solid residue dried at 110 ºC for 2 h and analyzed by physical and chemical methods. The liquor after filtration was analyzed for major and minor metals content.

After liquor colling the ammonium alum crystals ($NH_4Al(SO_4)_2 \cdot 12H_2O$) were precipitated. These crystals 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. Next, the crystals were dissolved in distilled water for iron removal by Purolite S957 resin. Resins were placed in 2M sulfuric acid for 3 h to converted it into the H^+ form. Fe batch sorption was performed by mixing a Purolite S957 resin with an ammonium alum solution at the ratio 1:100 in a plastic Erlenmeyer flask. The Erlenmeyer flask was agitated at 100 rpm with an ECROS PE-6300 laboratory shaker (LLC ECROSKHIM, Russia) at a temperature of 55 ºC for 2 h.

After filtration from resin, the solution was used for gibbsite precipitation by two methods: using ammonia water (NH_4OH) with and without seed addition. The alum solution was heated in laboratory glass on a magnetic stirrer to 90 ºC, stirring rate was 350 rpm. The precipitation process time was 2 h. Ammonia was added to the alum solution using peristaltic pump YW21-SP25 (YW FLUID, China) at a rate of 1 mL/min. Precipitation was completed at a solution pH = 7, then the solution was filtered, washed, and dried at 110 ºC for 4 h. Calcination gibbsite samples was carried out in a PM-1 muffle furnace (Plavka.Pro, Russia) at T = 900 ºC at 1 h. The samples of gibbsite and alumina were analyzed by physical and chemical methods.

2.3 Analytical Methods

Phase composition of the samples were measured by X-ray diffraction (XRD) using a Difrei-401 X-ray diffractometer (JSC Scientific Instruments, Russia) using a Cr-Ka radiation source and a 2θ range from 5º to 140º with 30 min exposure time. The operating mode of the X-ray source was set to 25 kW/4 mA. The mineral phases were analyzed by Match! 3 software. The surface morphology and elemental composition of samples were investigated by scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDX, Vega III, Tescan, Czech Republic). The metals concentrations in solutions and solid samples were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) using an atomic absorption spectrometer AA-240FS (Varian, Melbourne, Australia). The particle size distribution of samples was determined by laser diffraction method (LD) using Bettersizaer ST (Bettersize Instruments Ltd., China) and Zetasizer Nano ZS (Malvern, UK). The specific surface area of samples analysed by the Brunauer–Emmett–Teller method (BET) using NOVA 1200e (Quantachrome Instruments, FL, USA).

3. Results and Discussion

3.1 Bauxite High-Pressure Acid Leaching Process

At the first, during the bauxite acid leaching tests alum solution for further studying the behavior of impurities at the ion sorption, precipitation of gibbsite, and calcination of alumina was obtained.

During bauxite high-pressure leaching process (HPAL), the main Al phases - boehmite (AlOOH) and gibbsite ($Al(OH)_3$) and Hematite (Fe_2O_3) were completely dissolved. Non leached Al remains in aluminosilicates – kaolinite ($Al_2(Si_2O_5)(OH)_4$) and muscovite ($KAl_3Si_3O_{10}(OH)_2$) (Figure 1). Anatase (TiO_2) didn't leach and remains in the residue. Its content in residue, about 10 wt.% (Table 1). The Al extraction degree of HPAL was 88.75%.

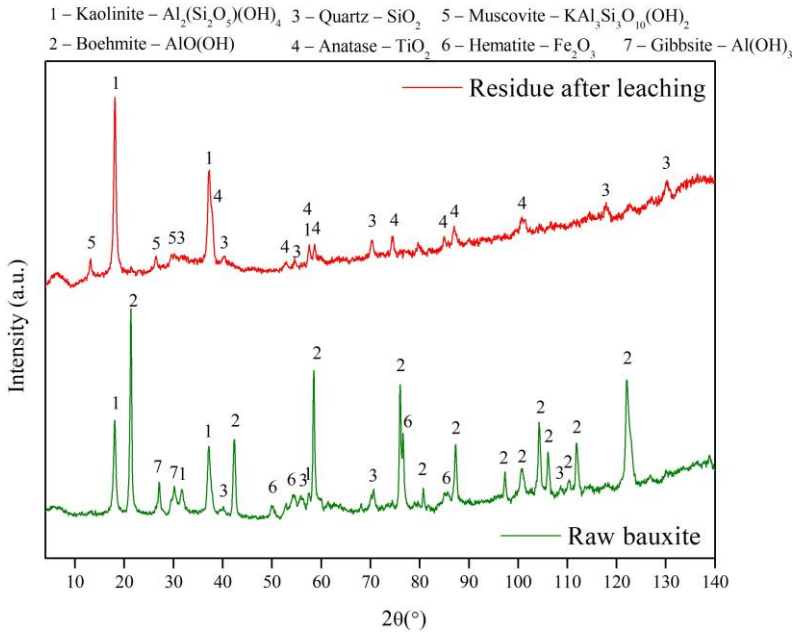


Figure 1. XRD patterns of the raw bauxite and residue after 40% NH_4HSO_4 + 3M H_2SO_4 leaching at T = 170 ºC (L:S = 10; τ = 90 min).

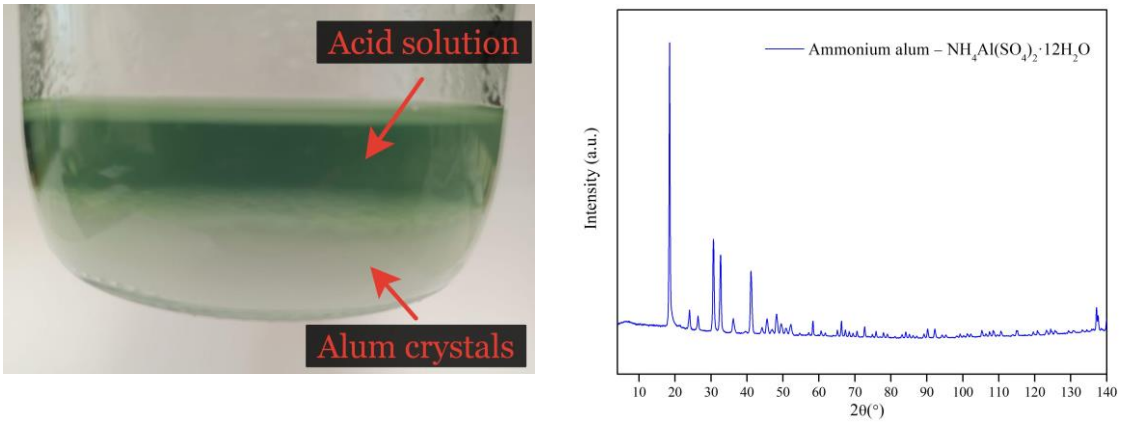
Table 1. Chemical compositions of raw bauxite and residue after HPAL process.

	Main components, wt. %									
	Al_2O_3	**SiO_2**	**Fe_2O_3**	**TiO_2**	**CaO**	**Cr_2O_3**	**MgO**	**Na_2O**	**K_2O**	**LOI***
Raw bauxite	53.30	17.80	6.52	2.57	0.68	0.52	0.75	0.04	0.23	15.60
Residue	16.15	59.79	1.24	10.17	0.50	0.35	0.28	0.11	0.73	10.62

*LOI – loss on ignition at 1000 ºC.

3.2 Ammonium Alum Crystallization and Purification

After pulp filtration, the ammonium alum solution was cooled to room temperature (25 ºC), while alum crystals were precipitated (Figure 2). The alum crystals were filtered from acid solution, washed by cold distilled water, and dissolved in distilled water for further iron sorption. The iron content in solution during sorption decreased more than 2 times from 241 mg/L to 94.1 mg/L (Table 2). The resin recovered only iron from solution, the chromium (Cr) content does not decrease and remains at the 5.9 mg/L. The loss of aluminum is about 5 %.



(a) **(b)**

Figure 2. Ammonium alum crystallization process: (a) acid solution and crystals; (b) XRD patterns of ammonium alum crystals.

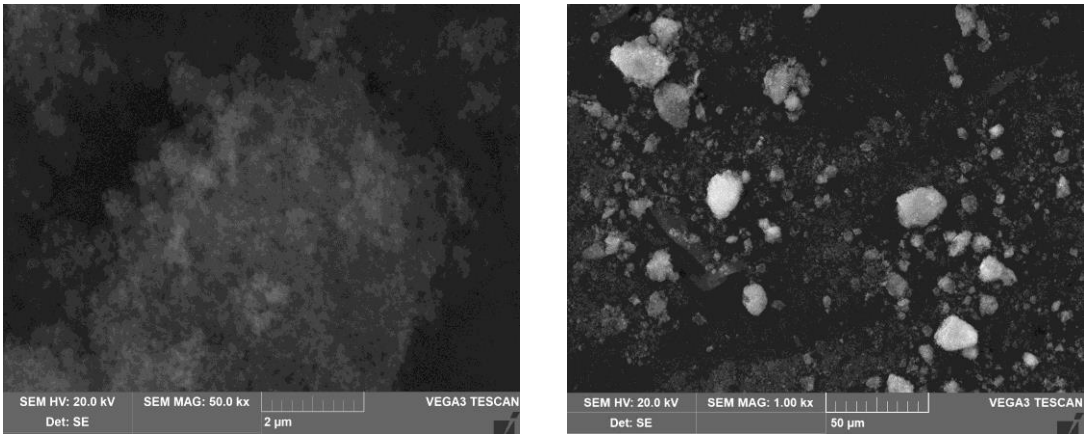
Table 2 The impurities concentration in the solution after bauxite HPAL process, ammonium alum washing water and alum solution (mg/L).

Sample	Al	Ca	Cr	Fe	K	Mg	Mn	Na	P	Si	Ti	V	Zn
Liquor after leaching	2560	462	321	3910	7.2	75.9	24.2	69.6	13.4	141	82.3	57.0	4.6
Ammonium alum washing water	3180	124	88	1280	0.5	20.0	6.4	15.4	3.5	37.3	21.5	14.8	1.2
Alum solution	3640	0.60	5.8	241	1.4	0.23	0.02	2.4	0.2	0.18	0.21	0.16	0.05
Alum solution after Purolite S957 resin sorption	3460	2.1	5.9	94.1	3.0	0.39	0.02	6.3	0.2	0.29	0.05	0.17	0.05

3.3 Gibbsite Precipitation Process

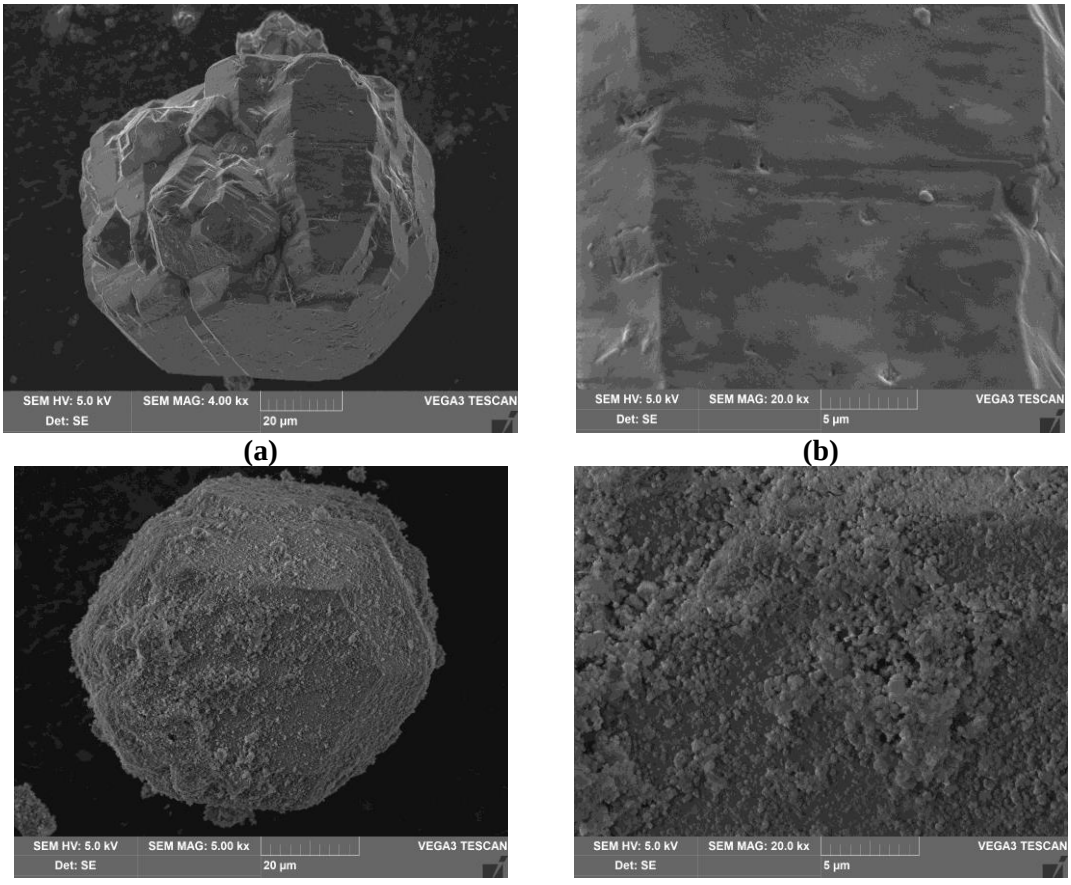
In this study, two methods for obtaining gibbsite from the alum solution were studied. The first method assumed a slow increase of the solution pH from 2.4 to 7 at T = 90 ºC during 2 h. The precipitated powder consisted of nanoparticles of gibbsite (Figure 3), which were combined into micron-sized agglomerates.

The second method involved adding a seed gibbsite to the alum solution. The precipitation process was carried out while keeping the pH of the solution at 3 for 2 h and then raised the pH to 7 for 30 min. As can be seen from Figure 4 that the nanoparticles of gibbsite cover the surface of the seed gibbsite particles.



(a) **(b)**

Figure 3. The SEM images of the nano gibbsite after precipitation process.



(a) **(b)**

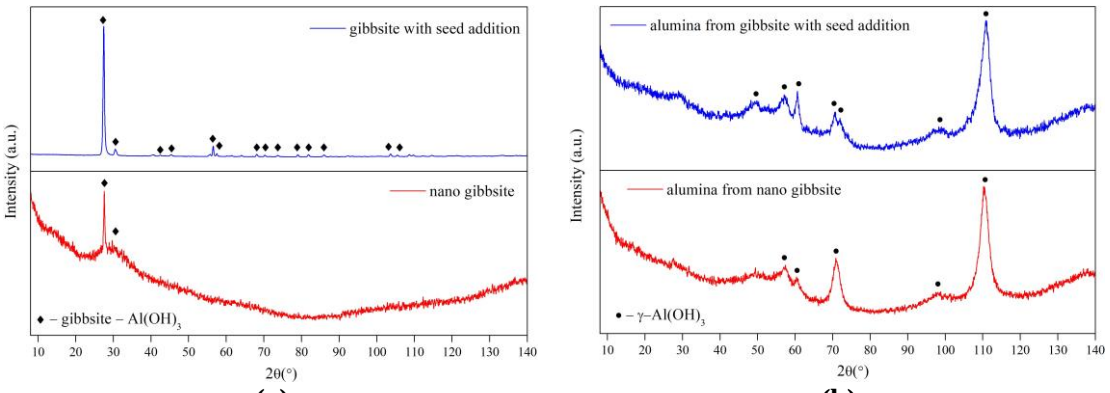
(c) **(d)**

Figure 4. The SEM images of the gibbsite samples: (a) seed gibbsite particle; (b) the surface of seed gibbsite particle; (c) gibbsite particle after precipitation process; (c) the surface of gibbsite particle after precipitation process.

3.4 Gibbsite Calcination for Alumina Production

Previous studies have shown that at higher temperatures of 1100 ºC, the main phase is the α-Al_2O_3 with a small amount of θ-Al_2O_3 [5]. So, the calcination of two samples of gibbsite was carried out at 900 ºC to obtain a γ-Al_2O_3. The XRD patterns of gibbsite and alumina samples were shown in

Figure 5. The nano gibbsite sample has a large amorphous component, however, after calcination process, the XRD patterns of both alumina powders are almost the same and contain 100% of γ-Al2O3.



(a) **(b)**

Figure 5. The XRD patterns gibbsite and alumina samples: (a) nano gibbsite and gibbsite with the seed addition; (b) alumina powder obtained from nano gibbsite and gibbsite with the seed addition calcination process.

During the precipitation of nano gibbsite from an alum solution, the powder size is 50-300 nm, further at the calcination process of these particles the larger agglomerates 500-1100 nm were obtained (Fig. 6). Moreover, gibbsite powder initially has a large amorphous part (Fig. 5a). After calcination the amorphous powder was crystallized, this fact leads to increase the particle size. The sample of gibbsite with seed addition practically did not change the particle size during calcination and was about 38.04 μm.

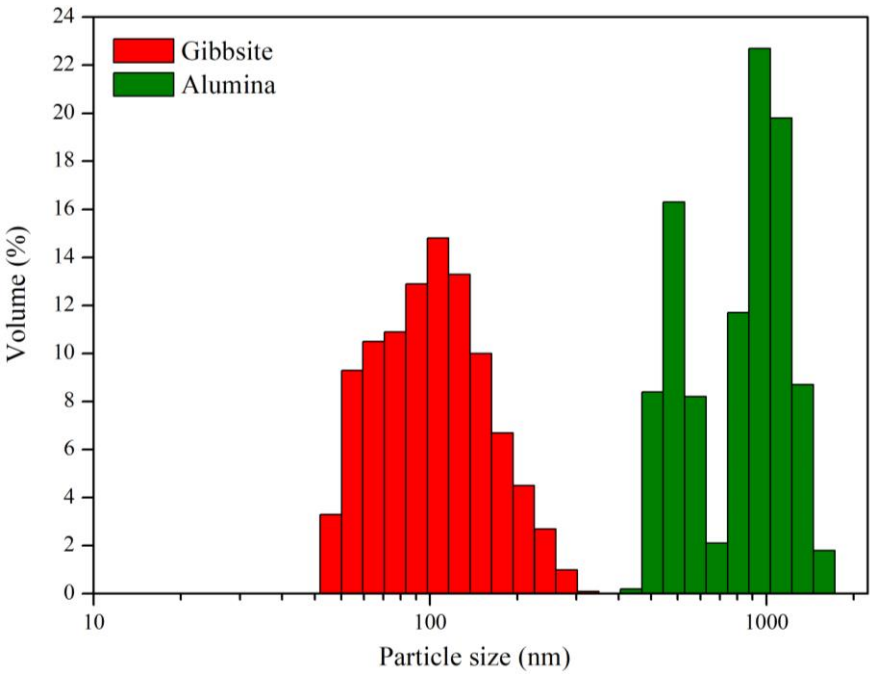


Figure 6. Particle size distribution (nm) of nano gibbsite and alumina powder after calcination at 900 °C.

Analysis of the specific surface area of the samples showed that their value increases significantly after calcination (Table 3).

Table 3. The specific surface area (BET) (m^2/g) of alumina powders.

Nano gibbsite	Alumina from nano gibbsite	Seed gibbsite	Gibbsite with seed addition	Alumina from gibbsite with seed addition
38.50	118.44	0.55	11.62	64.94

From the obtained data in terms of physical properties (specific surface area, particle size and phase composition) the sample obtained after using the seed gibbsite corresponds closely to sandy grade alumina. So, the samples of gibbsite after the precipitation process and alumina after gibbsite calcination were analyzed for the impurities content (Table 4).

Table 4. The impurities concentration (wt. %) in the experimental samples of gibbsite and alumina compared to Russian State Standards (GOST 30558-2017).

	Gibbsite with seed addition	Alumina from gibbsite with seed addition	Russian State Standard G-0 (GOST 30558-2017)
CaO	0.081	0.252	-
Cr_2O_3	0.009	0.013	0.002
Fe_2O_3	0.128	0.2	0.05
K_2O	0.182	0.29	-
MgO	0.002	0.025	-
MnO	0.0005	0.0001	0.002
Na_2O	0.284	0.48	0.5
P_2O_5	0.009	0.005	0.002
SiO_2	0.026	0.052	0.07
TiO_2	0.0008	0.001	0.007
V_2O_5	0.0018	0.004	0.005
ZnO	0.0063	0.01	0.03

As can be seen from the chemical composition of alumina, the Fe, Cr and P content was higher than this value in the Russian standards. Together with the low particle size compared to the Aluminum Smelters requirements (38.04 μm versus 60-90 μm), the experimental sample of alumina cannot be considered an analogue of the sandy grade alumina. Further research is needed to reduce the concentration of impurities, especially iron and chromium, as well as to study methods for growth of the particle size distribution.

4. Conclusions

In this article, the process of alumina production from Severoonezhsk bauxite using the bisulfate method was studied. The main methods of bauxite treatment: leaching, alum crystallization, iron recovery from alum solution by resin sorption, precipitation of gibbsite and calcination. The physical properties and chemical composition of the samples of gibbsite and alumina were analyzed. It has been shown that, during gibbsite precipitation without the addition of seed, nanoparticles were formed. They have a high specific surface area (118 m2/g), however, due to the very fine particle size (0.5-1.1 um), this powder cannot be used for subsequent electrolysis process. The seed addition allows precipitating nano gibbsite on the surface of the seed particles. However, after analyzing the behavior of impurities, it was shown that to correspond of the Russian State Standard of sandy grade alumina, it is necessary to reduce the content of Fe, Cr and P.

Acknowledgements

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5. References

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