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Extraction of Zirconium From Iraqi Bauxite Ore

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KEYWORDS

Bauxite Ore, Alumina Leaching, Bauxite Leaching, zirconium extraction.

ABSTRACT

This research is devoted to the study of the extraction of zirconium from Iraqi Bauxite Ore by using hydrometallurgical method. The chemical analysis was done to the bauxite ore by using X-ray florescence, X-ray diffraction and atomic absorption spectroscopy. Zirconium Extraction was performed via three stages; the first stage is leaching of bauxite with sodium hydroxide for alumina leaching. The second stage is leaching of zirconium species from the remained powder produced from stage one after washing with deionized water and, nitric acid (HNO3 solutions). The results of the first stage has reflected the recovery of 42.27 % of Al2O3 which has been leached 100°C temperature, 7.5 molar of NaOH, liquid to solid ratio of 20/1, and stirring rate 450 rpm. The highest leaching percent of zirconium (Zr%) from the red mud approached 98.48 % at 100°C temperature, 7 molar acid concentration, 120 min. contact time, solid to liquid ratio (S/L) of 16/1, and stirring rate of 450 rpm. 99.47% recovery of zirconium was accomplished from nitric acid solutions by use of 3molar tri-n-butylephosphate (TBP)in kerosene at ,contact time for 6 min, and organic to aqueous phase (O/A) of 4/1.

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1. INTRODUCTION

A bauxite ore is a naturally weathering heterogeneously product composed primarily of one or more hydroxide aluminum minerals. The main minerals are monohydrate boehmite (Al_2O_3-H_2O), trihydrated gibbsite (Al_2O_3-$3H_2O$) and oxide-hydroxide diaspore [α-AlO(OH)]. Also, it contains mixtures of different types of (Fe_2O_3) iron oxide, (TiO_2) titania, silica (SiO_2), aluminosilicate (clay, etc.), and various impurities in minor or little amounts. [1,2]. Zirconium as a rare element has been commercially produced in significant quantities about 1950 [3]. The main economic source of principal for zirconium is the zirconium mineral silicate zircon ($ZrSiO_4$). The second source zirconia (ZrO_2) is obtained from the mineral baddeleyite [4,5]. Due to the corrosion resistant and good mechanical properties at higher temperature and low thermal neutron absorption cross-section, zirconium alloys are preferred for structural materials and cladding in thermal neutron power reactors [6]. The bauxite - in Iraq, discovered in 1990s in northern Al-Husseiniat, the nature of these deposits was kinds of karst bauxite Alkhasafi. There are about (2,617,922) tons of Bauxite reverse with alumina contain (36.17%-41.1%) [7]. Bauxite ore used in this research contain 0.2455% to 0.3% of ZrO_2. El-Abdel-Aal [8] investigated the leaching kinetics of bauxite ore with sodium hydroxide, under various conditions of sodium hydroxide concentration, particle size of the ore, and temperature reaction on the leaching rate of Al_2O_3, around 99% of Al_2O_3 $Al_2O_3$was obtained at -200+270 particle size of ore, 250 g/L NaOH, with reaction time of 60 min and temperature reaction of 105 °C. The ratio of liquid -to- solid was maintained constant at 1:20.

Blazheva et al. [9] studied the zirconium extraction with tributyle phosphate (TBP) in organic diluent. The dependence of the distribution ratio of Zr on the concentration of TBP in the organic phase and the various concentrations of Zr and HNO_3 in the aqueous phase are evaluated. The extraction data and the infra-red spectra of the extracted zirconium complexes revealed that at least two kinds of extractable solvates zirconium nitrate with TBP are formed in extraction with 30% TBP and concentration of HNO_3 not exceeding 3M contains molecules of water. Shabana, and Haffz [10] studied the Zr(IV) extraction by tri-n-butylphosphate from HCl, HNO_3, HBr, and H_2SO_4 solutions, also from the mixtures of H_2SO_4 and acids halogen. It has been found that the extraction of Zr(IV) is increased by the addition of halogen acid to solutions of sulphuric acid. Also, the presence of acetone and water-miscible alcohols was found to enhance the extraction of Zr (IV) from HNO_3 and HCl aqueous solutions. Ajemba [11], optimized the leaching of alumina by sulphuric acid from Nteje clay and evaluated the influence of the acid concentration, ratio of solid-to-liquid, stirring speed, temperature calcinations and temperature leaching on the leaching process in order to improve the conditions employed in the batch process. The best conditions of leaching 81.87% of alumina experimentally was observed at 97oC, temperature of calcination is 675oC, ratio of 0.03 g/ml of solid- liquid, 2.97 mol/l concentration of acid, and speed of stirring 476 rpm.

2. EXPERIMENTAL WORK TEXT CITATIONS

Materials and methods

The Bauxite ore samples were supplied by the Iraqi geological survey from Al-Hussainyat area in Anbar province western Iraq as shown in Figure 1.

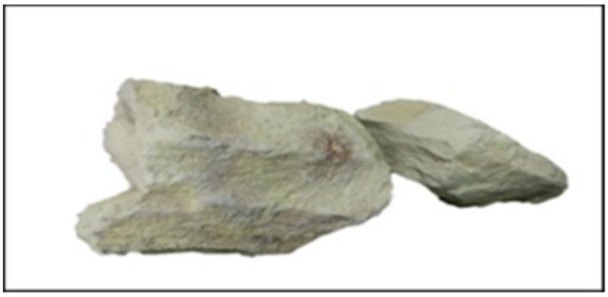

Figure 1: Bauxite ore rock

The received Bauxite ore rock samples were comminuted by laboratory jaw crusher type (retch-BB100) and ball mill type (retch-DM 200). It, has been performed in the minerals processing laboratory at the Department of Production Engineering and Metallurgy, University of Technology, Baghdad, Iraq. The sample was sieved for ten minute in a laboratory sieve shaker type (Retsch-AD60-01); using set of sieves with size (250, 212, 150, 105, 75, and 53) µm, -150+75 µm particle size was used for leaching experiments. XRF analysis of bauxite ore completed by (SPECTRO XEPOS) model at University of Baghdad, Department of Geology, Iraqi-Germany Laboratory as shown in Table I.

TABLE I: X-Ray fluorescence analysis of Iraqi Bauxite Powder

Element oxide	Concentration (%)
Al_2O_3	46.75
SiO_2	13.31
P_2O_5	0.4764
CaO	0.159
TiO_2	4..39
ZrO_2	0.2275
Fe_2O_3	1.76
L.O.I	0.27756
Total	67.366

The XRD type 6000 SHIMADZU and D2-PHASER, BRUKER Japan, was used for mineralogical analysis of sample carried out by Iraqi-Germany laboratory / department of geology; University of Baghdad Figure 2 shows the results of bauxite ore before leaching.

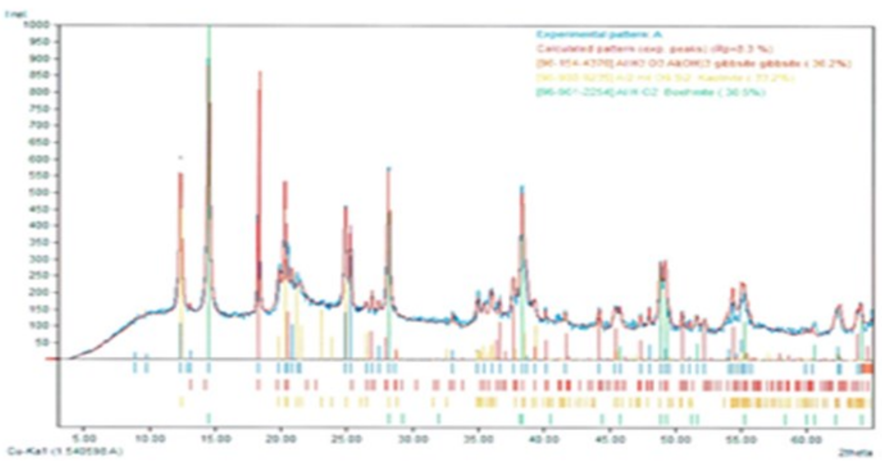

Figure 2: X-ray diffraction analysis of Iraqi bauxite ore

Gibbsite [Al $H_3O_3Al(OH)_3$] = 36.2%/ Kaolinite [A_{l2} H_4O_9 Si_2] = 33.2%/ Boehmite [Al H O_2] = 30.5%

Leaching has been done for bauxite of +75-150µm in leaching cell consist of 250 ml 3- neck round bottom glass with refluxing condenser and thermometer placed in the magnetic stirrer heating mantle. The slurry in the vessel is stirred by using Teflon coated magnetic. The solution used for leaching process is kept constant (100 ml) in all leaching experiments. After each experiment the ore is filtered by filtered papers. After that the residual is dried in oven at100^{o}C. Known weighted or known volume samples have been sent for XRF and atomic absorption analysis for zirconium and others. The atomic absorption spectroscopy type (nova - AA 350), was used to determine the dissolved Al_2O_3, ZrO_2 in solution of leaching and extraction process experiments at the laboratories of Ibn-Sina State Company, Bagdad, Iraq.

3. Results and Discussion

Leaching Process involves the extraction of zirconium is accomplished via three stages, firstly leaching of alumina using NaOH, the residue washed with deionized water, then zirconium was leached using nitric acid.

Stage one: leaching of alumina

I. Effect of NaOH concentration

Figure 3 depicts the influence of various concentrations of sodium hydroxide on the percentage of leaching with the range of (3.7, 5, 6.2, 7.5, and 8.7) M at 100oC. The leaching temperature of alumina was constant at 100oC chosen after studying the range of between 105°C - 290°C according to the type of bauxite ore [8]. The fixed time was 1hr, liquid to solid ratio 10/1, and the rate of stirring 450 rpm. The best leaching percent obtained is 30.5% at 7.5 M of sodium hydroxide then decreases probably due to the reverse reaction of equation-1.

$$2NaOH+Al2O3.3H2O = 2NaAlO2 + 4H2O \quad (1)$$

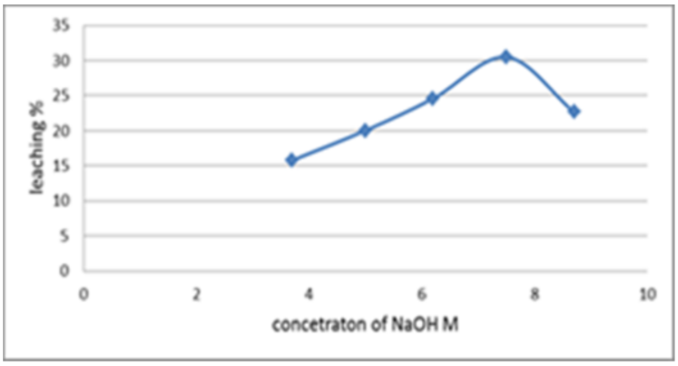

Figure 3: The relationship between leaching (%) and the concentration of NaOH(M).

II. Effect of time

Different contact time intervals have been tried for the leaching of alumina i.e., (60, 120, 180, 240, and 360) min. The highest percentage of leaching approached 34.6% at 6hrs as shown in Figure 4.

The long period required reflects the slow reaction kinetics under the studied conditions, however, the reaction rate might be improved under high pressure in autoclave environment.

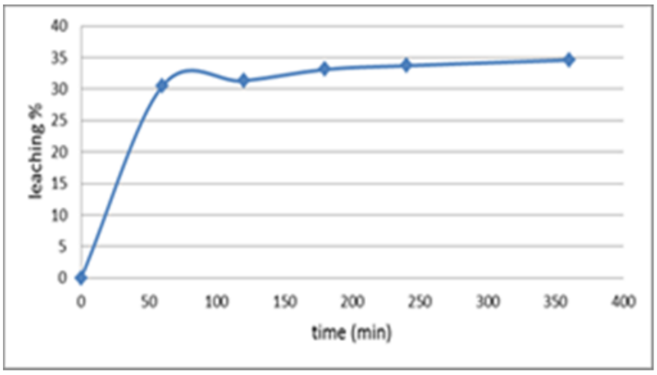

Figure 4: The Effect of time on percentage of leaching for alumina at, 100°C, NaOH 7.5 M, liguid to sloid ratio 10/1 and rate of stirring 450 rpm

III. *The influence of liquid to solid ratio*

Many sets of experiments performed at (10/1, 20/1, 30/1, 40/1, and 50/1). The best leaching percent obtained approached 42.27% at the 20/1 L/S ratio. Table II represents the result of the leaching process. At the end of these experiments, the highest leaching percentage of alumina is 42.27% at contact time 60 min, temperature 100°C, NaOH 7.5 M, L/S ratio 20/1, and stirring rate 450 rpm. High consumption of the leaching base can be ascribed to the presence of high content of silica in the Iraqi bauxite [12].

TABLE II: The effect of L/S ratio on the leaching of alumina at; 100°C, NaOH 7.5 M, time 60 min and stirring rate 450 rpm

NO	L/S ratio	leaching

1	10/1	30.58
2	20/1	42.27
3	30/1	27.65
4	40/1	19.41
5	50/1	17.87

4. Stage two: leaching of Zirconium

I. The effect of temperature

Figure 5 shows that zirconium leaching increases with increasing temperature at range studied i.e.,25, 50, 75, and 100 °C, in the presence of the concentration of nitric acid 10 M, contact time 90 min, and L/S ratio 25\1, and stirring rate 450 rpm., approaching percentage of leaching 47.84%.

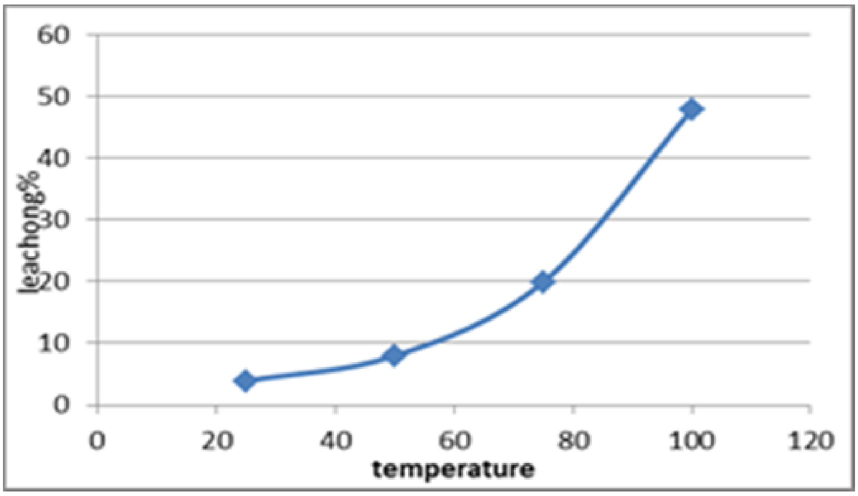

Figure 5: Relationship between leaching (%) and temperature

II. The Effect of acid concentration

Five different concentrations are selected to establish the maximum leach ability of zirconium reached to the higher percentage 67.5% at 7M acid concentration. By nitric acid i.e., 1, 3, 5, 7, and 9 M. Experiments are implemented under the conditions of temperature 100°C, time 60 min, L/S ratio 25/1, and the speed of stirring 450 rpm. The experimental results are illustrated in Figure 6. From this figure, it can be concluded that the leaching efficiency of zirconium increases as the acid concentration increases. It reached a higher percentage of 67.5% at 7M acid concentration.

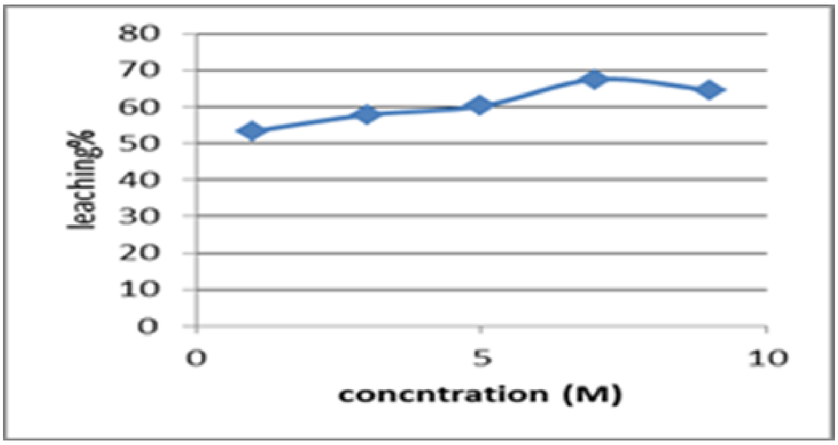

Figure 6: Relationship between acid concentration and leaching% of zirconium at; temperature 100°C, L/S ratio 25/1, time 60 min and stirring 450 rpm.

III. Effect of time

Figure 7 shows the effect of contact time on the ZrO2 leaching percentage. The studied times are 30, 60, 90,120, and 150 min at the concentration of 7M, temperature of 100^{o}C, L/S ratio of 25/1, and stirring rate of 450 rpm. The best leaching percent is 76.95% at 120 min. The reason for increasing the leaching percentage with the increase in leaching time is due to that the increase in time increases the solubility of the solution by contacting with the solids, and giving sufficient time for the diffusion of the solution in the solids, thus increasing the reaction rate.

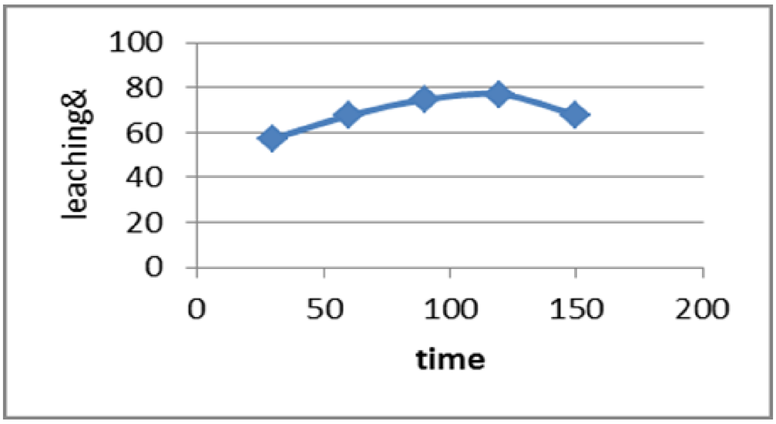

Figure 7: Effect of time on the leaching of zirconium at; temperature 100°C, L/S ratio 25/1, acid concentration 7M and stirring rate of 450 rpm.

IV. Effect of L/S ratio

L/S ratio affected the process of leaching. It was selected as (100/1, 50/1, 33/1, 25/1, 20/1, and 16/1) with the following conditions obtained from the previous experiments: (the acid concentration 7M, temperature 100 °C, time 120 min, and stirring speed 450 rpm). The highest leaching percentage is 98.48% at L/S ratio of 16/1. The results of the effect of L/S on the leaching % are represented in Table III.

TABLE III: Effect of L/S ratio on the leaching of zirconium at; 100^{o}C, acid concentration 7 M, time120 min and stirring rate of 450 rpm

NO.	L/S ratio	leaching (%)
1	100/1	60.20
2	50/1	68.58
3	33/1	77.35
4	25/1	76.95
5	20/1	84.13
6	16/1	98.48

5. Stage Three: (Liquid–liquid) Extraction of Zirconium

After leaching with nitric acid, the solution bearing Zr ion is subjected to tributyl phosphate(TBP)-kerosene extraction for the separation from other available ions according to the following relation:

$$Zr4+ +4NO3- + (TBP)org. = \{Zr(NO3)4TBP\}org \quad (2)$$

I. Effect of TBP concentration

The best result of the Zr extraction by (TBP) in kerosene is 97.5% produced by (3 M) from different concentrations ranges of (1, 2, 3, 3.5) M. The organic to aqueous ratio is 1/1, and the contact time is 8 min. Figure 8 shows the relation between the concentration of TBP and extraction % (Ex %) of Zr. The extraction increases with increasing TBP concentration.

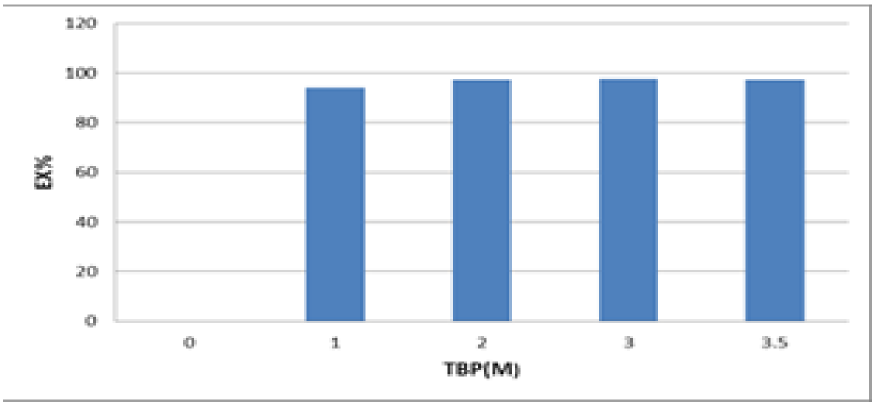

Figure 8: The influence of TBP concentration on the extraction of Zr % at; organic to aqueous 1/1 and time 8 min

II. Influence of organic to aqueous ratio (O/A)

Experiments performed at 1/1, 2/1, 3/1, 4/1, 1/2, 1/3, and 1/4 of O/A ratio to reach optimum of 99.4% at (O\A) ratio of 4/1, TBP concentration is 3 M, and the contact time 8 min. The influence of (O/A) ratio on the extraction of Zr % is demonstrated in Table IV.

TABLE IV: Effect of O/A on the extraction % of ZrO_2 at; TBP 3M and time 8 min

NO.	O/A ratio	EX (%)
1	1/1	97.5
2	2/1	98.53
3	3/1	99.12
4	4/1	99.4
5	1/2	95.26
6	1/3	94.40
7	1/4	91.56

III. Effect of contact time

The extraction of zirconium was performed at different contact time intervals of 2, 4, 6, 8, 10, and 12 min. The best results obtained approached 99.47% at 6 min. Figure 9 shows the influence of the period of time on the removal of Zr by TBP. The concentration of TBP and O/A ratio fixed at 3 M, and 4/1, respectively. The results show that time is not critical parameter reflecting fast kinetics extraction reaction.

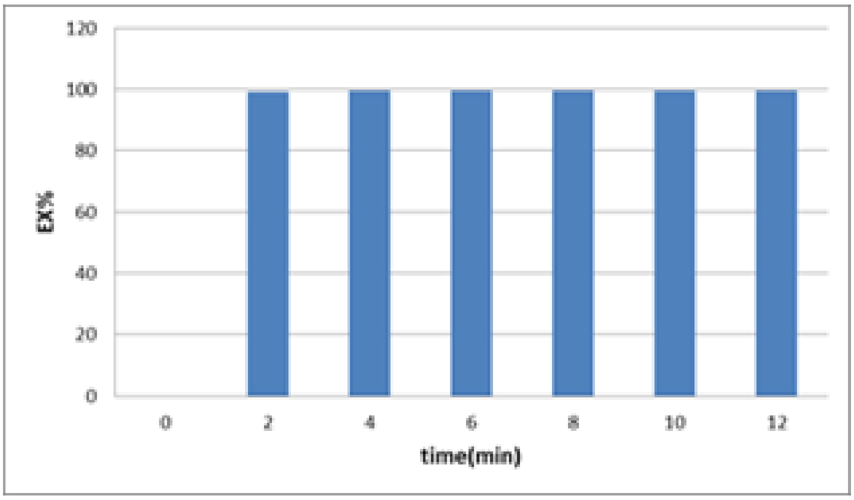

Figure 9: Effect of time on the extraction % of Zr at; organic to aqueous ratio 4/1 and TBP concentration 3M

6. Conclusions

The main conclusions which can be realized from the present work are:

1. The highest leaching percent obtained is 42.55% of alumina from the Iraqi bauxite ore - Al-Husseiny at region with NaOH, under the conditions of temperature 100°C, NaOH concentration 7.5 M, contact time 60min, L/S ratio20/1, and stirring rate 450). Further work should be done using high pressure autoclave reactions.
2. The highest percentage leached of Zr is 98.48 % from the red mud (residue) using nitric acid under the conditions (temperature 100°C, acid concentration 7M, time 120min, L/S ratio 16/1, and stirring rate 450). Nitric acid proved to be good leaching agent for Zr as it acts effectively to keep zirconium ions (Zr4+) stable in the aqueous solutions.
3. Highest extraction of zirconium (Zr %) is obtained by use of tri-n-butylphsphate (TBP) dissolved in kerosene under the conditions of (TBP concentration 3M, time 6min, and O/A ratio 4/1). Zirconium cannot be directly leached from bauxite ore, treatment with NaOH paved for the red mud formation and Zr leaching with nitric acid.

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