Cleaning Disposal of High-Iron Bauxite Residue (Red Mud) Using Hydrochemical Conversion of Goethite to Magnetite

Mamodou Malal Diallo[1], Andrei Shoppert[2], Irina Loginova[3], Marie Constance Beavogui[4] and Dmitry Valeev [5]
1. Bachelor student
2. Professor (assistant)
3. Professor
Department of nonferrous metals metallurgy, Ural Federal University, Yekaterinburg, Russian Federation
4. Laboratoire de Recherche Appliquée en Géoscience et Environnement, Institut Supérieur des Mines et Géologie de Boké (ISMGB), Boke, Guinea
5. Laboratory of Sorption Methods, Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation
Corresponding author: a.a.shoppert@urfu.ru

Abstract

In this paper, the hydro-chemical conversion of goethite to magnetite process for treating high-iron bauxite residue (red mud) was investigated, and the optimum conditions of alumina extraction as well as the enrichment of iron minerals were verified. Results show that the magnetization of Al-goethite in the presence of Fe^{2+} accelerates its conversion to magnetite with the simultaneous Al release from the solid matrix. After ferrous oxide was added directly as $FeSO_4$*7H_2O at the ferrous sulfate to bauxite residue ratio of 1:1 at 120 °C for 150 min in the alkaline media, the alumina extraction ratio reaches 97.13 % for sand and 89.13 % for bauxite residue and the grade of iron (total iron in the form of iron element) in the residue can be enriched to 69.55 % for sand and 58.31 % for bauxite residue. The obtained iron-rich residue can be used as a pigment-quality magnetite or in the steel industry.

Keywords: Red mud, High-iron, Al-goethite, Conversion, Magnetite.

1. Introduction

The bauxite residue (BR, red mud) production accounted for more than 200 million tonnes per annum [1]. BR is formed during the Bayer process used for alumina production worldwide via the alkaline method of leaching. As a result, BR contains a high amount of caustic alkali which makes this waste highly corrosive. In addition, the concentration of heavy metals after alumina extraction can be doubled in BR. Because its high toxicity and corrosivity, the BR utilization rate is very low, and it is stockpiled in large ponds.

Nevertheless, BR contains a high number of valuable components, such as iron, rare earth elements (REE), vanadium, titanium, etc [2]. The extraction of these elements from BR together with the reduction of its toxicity can be economically and ecologically beneficial. For example, BR produced during the processing of the Fria bauxite deposit in Guinea contains a very high amount of iron: from 40 % of the iron in BR to 55-60 % of the iron in sands formed by the gravity method of separation after digestion of bauxites on the Friguia alumina refinement.

Many methods of iron extraction from BR have been developed to date. These methods can be divided into pyro- and hydrometallurgical. Pyrometallurgical methods include magnetic separation after preliminary reductive roasting, reductive sintering with the different fluxes, and the smelting of BR with a reducing agent to obtain pig iron [3]. The major disadvantage of these methods is the high energy consumption because the temperature of these processes can be as high as 1000-1750 ˚C.

In the recent work of Li et al. [4,5], and Pasechnik et al. [6], it was shown that hematite from BR can be transformed into magnetite during a hydrothermal reduction in the presence of iron, Fe^{2+}, and OH^- ions (Equation (1)-(3)).

$$Fe + H_2O + OH^- = HFeO_2^- + H_2 \quad (1)$$

$$Fe^{2+} + 3\ OH^- = HFeO_2^- + H_2O \quad (2)$$

$$Fe_2O_3 + HFeO_2^- = Fe_3O_4 + OH^- \quad (3)$$

Furthermore, Zhou et al. [7] showed that the addition of Al during high-temperature digestion of high-iron BR, obtained after digestion of Guinea’s high-iron bauxites, not only transforms iron into hematite covered by magnetite but also accelerates Al extraction from Al-goethite. However, high-pressure leaching at a temperature of 270 °C is needed for the formation of the iron-enriched residue with an iron content of 56 %.

In this work, a novel method of atmospheric pressure reduction of Guinea’s high-iron BR using $FeSO_4$ was proposed. The optimum conditions of alumina extraction as well as the enrichment of iron minerals were verified. The solid residue was characterized using X-ray diffraction (XRD), SEM-EDS, and spectrophotometry methods.

2. Methods and Materials

The bauxite residue and the sand used in this research were obtained from Friguia alumina refinery in Guinea. The chemical compositions of BR and the sand are shown in Table 1. Other reagents, NaOH and $FeSO_4*7H_2O$ were of analytical grade. Sodium alkaline solutions with the Na_2O concentration 330-400 g L^{-1} were prepared by dissolution of NaOH in distilled water.

Table 1. Chemical compositions of bauxite residue and sand from Friguia alumina refinery, Guinea.

Sample	Fe	Si	Ti	Al	Na	O	Other
Bauxite residue	41.7	4.25	4.36	12.34	4.53	30.68	2.14
Sand	56.23	0.77	1.38	5.55	1.26	33.80	1.01

The extraction of Al by NaOH and conversion of goethite to magnetite was carried out in the thermostated 0.5 L stainless steel reactor. The reactor has openings for overhead stirring as well as for temperature control and the recycling of evaporated water through a water-cooled condenser. The stirring speed in all experiments was 300 rpm; the liquid to BR ratio (L:S ratio) was 10; the molar ratio of Fe^{2+} to Fe_2O_3 in BR and sand according to Equation (3) was equal to 1. The BR and sand together with the iron sulphate were added to the solution with the Na_2O concentration from 330 g L^{-1} to 400 g L^{-1} that makes it possible to use atmospheric leaching process even at a temperature 120 °C. Temperature of the leaching was varied from 100 to 120 °C; leaching time – from 1 to 5 h. After leaching, the pulp was filtered; the solid residue was dried at 110 °C for 8 h before analysis using powder X-ray fluorescence spectrometry (XRF) with an Axios MAX spectrometer (Malvern Panalytical Ltd., Almelo, The Netherlands), and X-ray diffraction (XRD) using a Difrei-401 diffractometer (JSC Scientific Instruments, Saint Petersburg, Russia) using a Cr-Kα radiator with 2θ angles ranging from 15 ° to 140 °. The operating mode of the X-ray source was 25 kW/4 mA with 30 min of exposure time. Match 3 software was used to process the diffraction data.

To exclude the mutual influence of factors on each other and to reduce the number of experiments, a Box-Benken experimental design created in the Statistica software was used in this research. The design is formed by 3 blocks of 15 experiments with varying parameters at three levels, as output parameters were the extraction of aluminum into solution, and the concentration of iron in the solid residue. Statistical-based automated neural network (SANN) was used for modeling Al extraction and goethite transformation. SANN is an artificial intelligent method that adjusts the result of modelling until the desired quality is obtained. “STATISTICA 13” software was used for SANN modelling via a multilayer perceptron (MLP) method.

The calculation of the magnitude of the blackness (My) is based on one of the values of the color coordinates - Y (brightness) that was determined using spectrophotometer at observers angle 10 ° (Equation (4)):

$$M_y = 100 \cdot \log\left(\frac{100}{Y}\right) \tag{4}$$

This determines only the degree of lightness/darkness of the sample without taking into account the color shade. Since the shade of black affects the visual assessment, the degree of blackness, depending on the shade, it was calculated as follows (Equation (5)):

$$M_c = 100 \cdot \left(\log\left(\frac{Xn}{X}\right) - \log\left(\frac{Zn}{Z}\right) + \log\left(\frac{Yn}{Y}\right)\right) \tag{5}$$

The Mc value describes a higher blackness if there is a blue shade (X), and a lower saturation if the shade is brownish (Z).

3. Results and discussion

To evaluate the effect of different leaching parameters on the extraction rate of Al and the Fe, Na_2O content in the solid residue, the leaching experiments were made according to the described methodology. Then, based on the experimental results, the neural network model of the process was obtained. The response surfaces of the model constructed by varying time, temperature, and the Na_2O concentration in the leaching process of the BR are shown in Figure 1.

The major effect (Figure 1a and Figure 1b) on Al extraction degree is caused by leaching time and temperature. Figure 1a shows that before 2.0-3.5 h of leaching Al extraction degree is increasing, after 3.5 h at 100 °C and 3 h at 110 °C Al begins to precipitate in the form of desilication product that can be confirmed by the increased content of Na_2O in the solid residue after 4 h of leaching (Figure 1e and Figure 1f). Due to the desilication product precipitation, the iron content in solid residue begins to decrease after 4 h of leaching (Figure 1c and Figure 1d). Nevertheless, a very high alumina extraction degree was obtained after 2 h at all the temperatures– more than 80 %. The total iron content in the solid residue can be increased from 41.7 (Table 1) to 56 % after 2.5 h of leaching at 120 °C (Figure 1c). The effect of Na_2O concentration in the solution on alumina extraction and on Na_2O content in the solid residue was very low (Figure 1e and Figure 1f).

Because of the low effect of Na_2O concentration in the solution on BR reductive leaching, it isn’t shown for sand (Figure 2). According to Figure 2a, the major effect on Al extraction is caused by leaching time, and the very high extraction degree was obtained after 1.5 h of leaching at 120 °C and C_{Na2O} 360 g L^{-1} – more than 95 %. However, the highest iron content in the solid residue is obtained after 2.5 h of leaching. Therefore, the optimal leaching parameters of sands and BR can be as follows: temperature = 120 °C, C_{Na2O} = 360 g L^{-1}, leaching time = 2.5 h. The content of Fe in the sands solid residue at these parameters was higher than 70 %, whereas Na_2O content was lower than 0.5 %. Such a product can be used as pigment-quality magnetite.

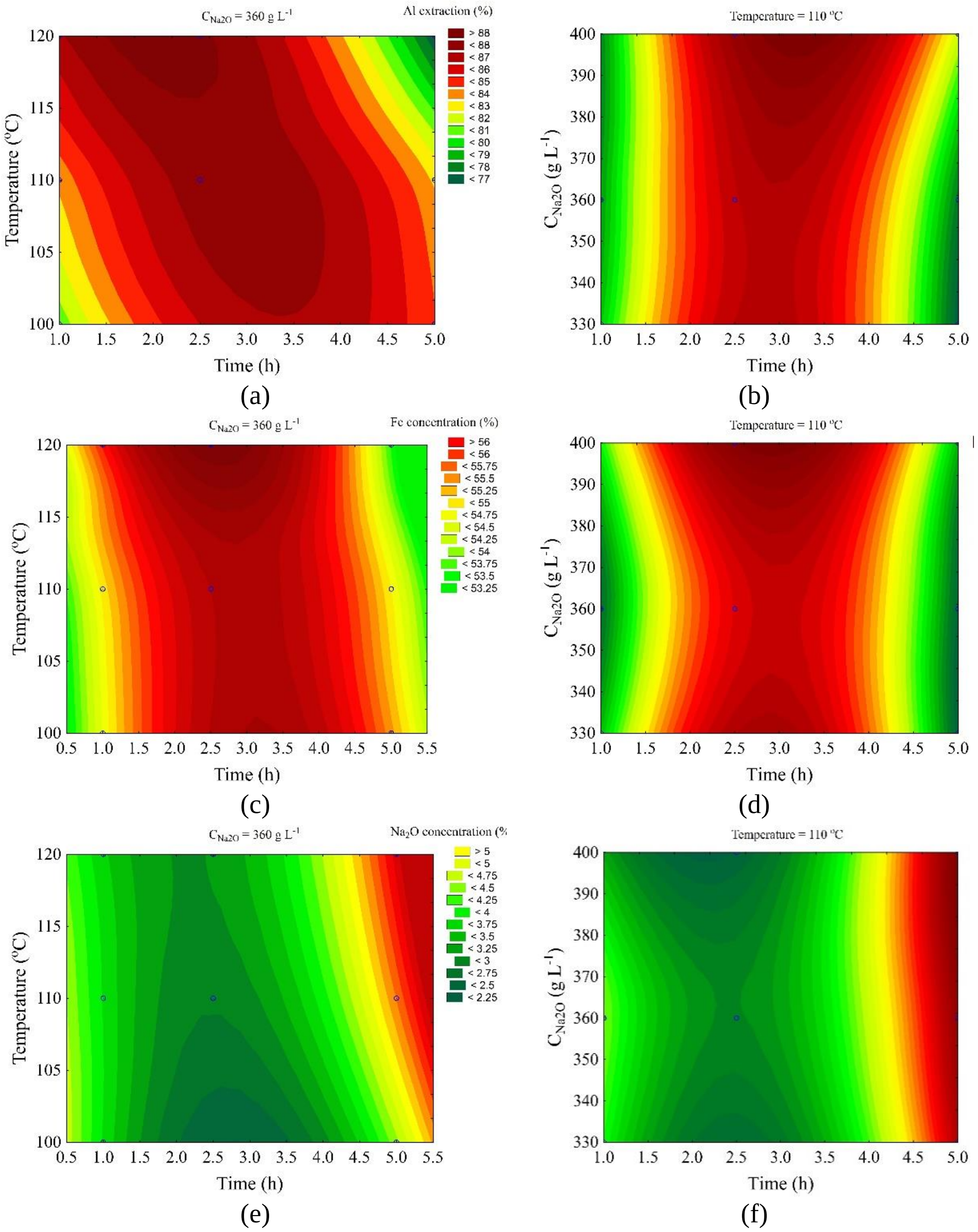


Figure 1. Neural network response surfaces for effect of time and temperature on the Al extraction from BR (a); effect of time and Na_2O concentration on the Al extraction from BR (b); effect of time and temperature on the Fe content in the solid residue (c); effect of time and Na_2O concentration on the Fe content in the solid residue (d); effect of time and temperature on the Na_2O content in the solid residue (e); effect of time and Na_2O concentration on the Na_2O content in the solid residue (f).

One of the most important parameters of the pigments is jetness. The effect of leaching time and temperature on the jetness of the magnetite concentrate obtained after the reductive leaching of sand is shown in Figure 2d. According to this data, 5 h of leaching is necessary to obtain the product with a jetness higher than 200. However, modern pigments can have jetness higher than 400. Therefore, there is a dilemma in obtaining high quality product (high jetness) with low impurities amount, because after 2 h of leaching, the Na_2O content increases to 2.5 %

One of the possible solutions to this problem is double leaching, where aluminum and silicon are removed with a partial transfer of goethite to magnetite at the first stage, and the product is subjected to “curing process” in a pure alkaline solution to obtain the required degree of blackness at the second stage.

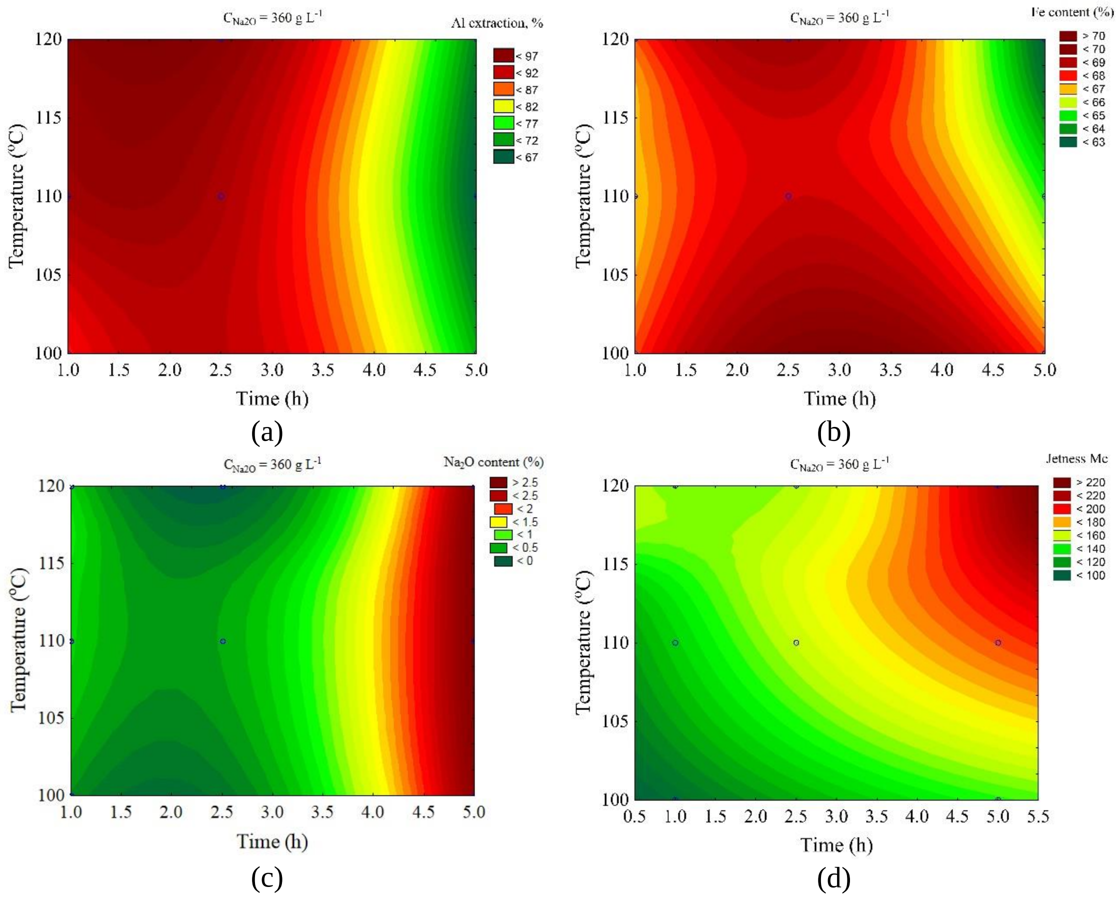


Figure 2. Neural network response surfaces for effect of time and temperature on the Al extraction from sand (a); effect of time and temperature on the Fe content in the sand residue (b); effect of time and temperature on the Na2O content in the sand residue (c); effect of time and temperature on the jetness (d).

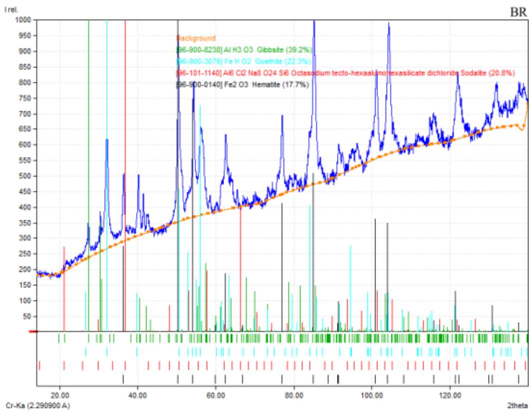
After the reductive leaching for 150 min at the ferrous sulfate to bauxite residue ratio of 1:1 and 120 °C in the alkaline media, the alumina extraction ratio reaches 97.13 % for sand and 89.13% for bauxite residue. The grade of iron (total iron in the form of iron element) in the residue can be enriched to 69.55 % for sand and 58.31 % for bauxite residue at these conditions. The chemical compositions of the solid residues obtained after BR and sand leaching at optimal parameters are shown in Table 2.

Table 2. Chemical compositions of solid residues obtained after reductive leaching.

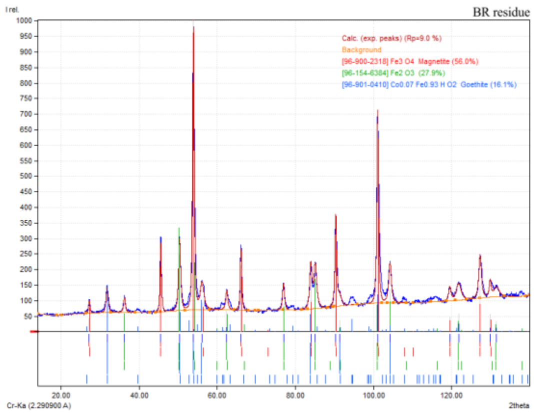
Sample	Fe	Si	Ti	Al	Na	O	Sc	Other
BR solid residue	58.31	2.06	3.92	1.33	1.45	31.35	0.006	1.58
Sand solid residue	69.55	0.34	1.01	0.15	0.24	27.81	0.005	0.90

As can be seen in Table 2, the solid residue obtained after reductive leaching of sand is very pure: Na and Al contents are lesser than 0.25 %. The content of Si and Ti are also smaller than in traditional bauxite residues. However, the contents of Na, Ti, Si and Al in the solid residue obtained after BR leaching are higher which makes it difficult to use this product as a pigment. The high Na content will also interfere with its use for iron production. Therefore, preliminary leaching of Sc by acid, for example, or the lime causticisation should be used before disposal. The P and S content in this product also are lower than 0.1 % (not shown in Table 2).

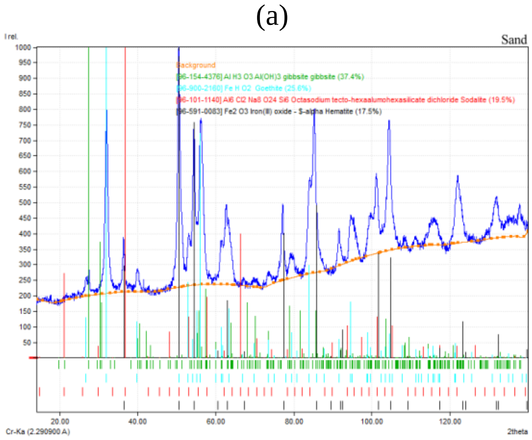
To evaluate why there is such difference in the results obtained using BR and sand, the XRD pattern of the solid residues were investigated (Figure 3). Figure 3a and Figure 3c show that there are differences in hematite, goethite and gibbsite content in BR and sand. Higher amount of hematite in BR results in the incompleteness of the process (the formation of magnetite from goethite is a faster process from view of thermodynamics). Also, there is some amount of sodalite in BR that will not dissolve in the alkaline media without lime addition that leads to the higher Na content in residue.



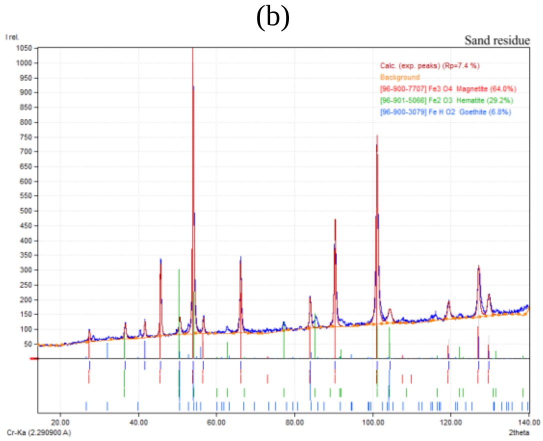
(a)



(b)



(c)



(d)

Figure 3. XRD patterns of the BR (a); solid residue obtained after BR leaching at optimal conditions (b); sand (c); solid residue obtained after sand leaching at optimal conditions.

4. Conclusions

In this study, the novel method of high-iron bauxite residues from Friguia alumina refinery treatment by low-temperature leaching in the presence of Fe^{2+} was investigated. Using machine learning with ANNs for analysis of the Al extraction degree, Fe and Na_2O content in residue showed that at optimal parameters (T = 120 ºC; L:S = 10; τ = 150 min, C_{Na2O} = 360 g L^{-1}), the alumina extraction degree reaches 97.13 % for sand and 89.13% for bauxite residue. The grade of iron (total iron in the form of iron element) in the residue can be enriched to 69.55 % for sand and 58.31 % for bauxite residue. Extremely low impurities content in the solid residue obtained after sand leaching and the high blackness degree makes it good alternative for pigment production. The difference in extraction degree and the total iron content in the solid residues obtained from sand and BR can be attributed to the higher amount of hematite and sodalite in BR. Sc acid leaching or lime causticisation can be used to reduce sodalite content in BR before disposal in iron production.

Acknowledgements

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5. References

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