WASTELESS PROCESSING OF RED MUD BY HYDROGARNET TECHNOLOGY

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Abstract

The current alumina production of Kazakhstan by the consecutive Bayer-sintering process becomes less profitable and requires modernisation. We have developed technology, which allows wasteless recycling of red mud by a hydrochemical method with the possibility of obtaining gallium and vanadium and also non-alkali hydrogarnet mud, suitable for use in construction, and producing pig iron and titanium-containing slag. As raw material Kazakstan's Koktalsk group gibbsite bauxite deposits with resources of 300 million tonnes was used. Red mud processing in an autoclave at 240 °C with liquor with high Na_2O/Al_2O_3 molar ratio in the presence of lime with obtaining of hydrogarnet mud, aluminium, sodium, vanadium and gallium concentrated in liquor. Removing aluminium was about 70 % and 95-98 % alkali. Liquor with medium Na_2O/Al_2O_3 molar ratio was conversed by adding $Ca(OH)_2$ in liquor with high Na_2O/Al_2O_3 molar ratio by synthesis of tricalcium aluminate hydrate (TCAH), with subsequent decomposition in soda bicarbonate liquor. Decomposed liquor carbonised in two stages, it generates alumina-carbonate precipitate which proposed to extract gallium and vanadium. Hydrogarnet sludge almost doesn't contain alkali and consist less aluminium oxide and more calcium oxide than red mud. Direct reductive sintering of hydrogarnet mud mixed with charcoal without fluxing additive in a muffle furnace at 1600-1650 °C was studied. As a result of sintering was good separation products self arenaceous slag phase and iron. Extraction of iron in cast iron was 84.6 %.

Introduction

Kazakhstan has a large amount of research on the development hydroalkali method of processing red mud by hydrogarnet technology in recent years.[1]

Treatment of red mud by autoclave leaching by the definite conditions using high modulus alkaline solution in the presence of lime and active multicomponent additive is synthesised of calcium compound - mostly ferruginous hydro-garnet

($3CaO \cdot Fe_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), which doesn't contain aluminium and alkali. Its excludes formation of aluminium hydrogarnet ($3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$).[2,3]

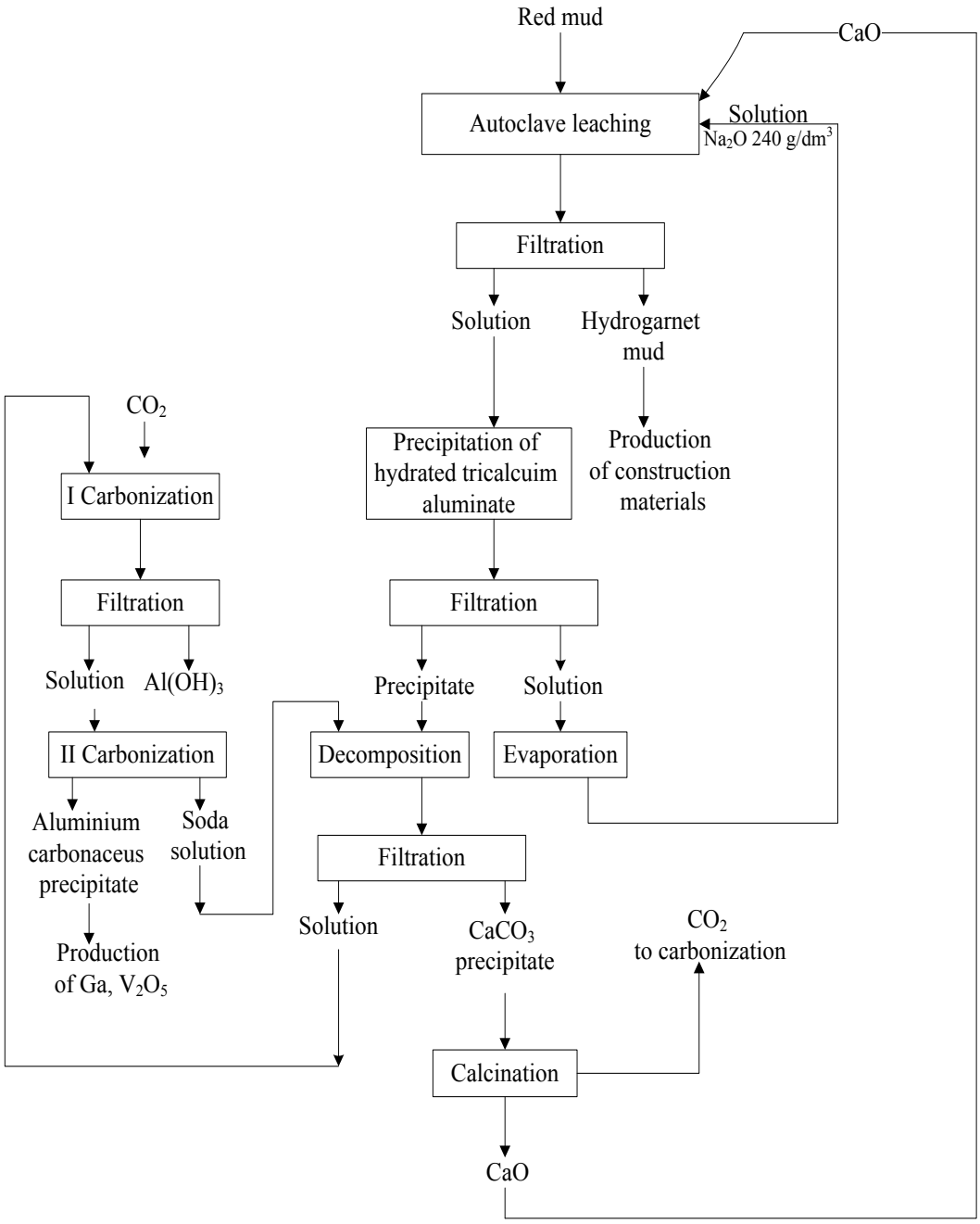

Figure 1: Technological scheme of hydro-garnet process for red mud

A red mud sample from Koktalsk deposit (Republic of Kazakhstan) which was obtained by the Bayer process for high ferruginous bauxite was used in this study. Koktalsk deposit bauxites rate as perspective raw material in alumina production.[4,5]

The Koktalsk deposit bauxites was determined to contain: 39.53 % Al_2O_3, 6.18 % SiO_2, 23.12 % Fe_2O_3, 4.37 % TiO_2 and 1.1 % CaO, μ=6.396.

The red mud sample was determined to contain: 7.33 % NaO, 10.47 % Al_2O_3, 11.19 % SiO_2, 46.95 % Fe_2O_3, 7.9 % TiO_2, 6.33 % CaO.

A high-modulus solution (Na_2O 285.0, Na_2CO_3 11.4, Al_2O_3 14.65, SO_3 4.23, SiO_2 0.024, α_k = 32.0) was used for autoclave leaching of red mud sample in the presence of lime-clinker suspension at a liquid-to-solids (L/S) ratio of 4.

As a result of autoclave leaching of red mud hydrogarnet sludge and middle modulus solution (165.35 g/dm^3 Na_2O, 7.59 g/dm^3 Na_2CO_3, 24.24 g/dm^3 Al_2O_3, 3.52 g/dm^3 SO_3, 0.05% SiO_2, α_k = 11.4) was produced.

Table 1: XRD pattern of the hydrogarnet mud

Compound Name	Formula
Hematite	Fe_2O_3
Andradite (hydrated)	$Ca_3(Fe_{0.87}Al_{0.13})_2(SiO_4)_{1.65}(OH)_{5.4}$
Katoite, syn	$Ca_3Al_2(O_4H_4)_3$
Magnetite, syn	Fe_3O_4

As a result of autoclave leaching of red mud by hydrogranet technology 98 % Na_2O regenerated, 64.9 % of red mud was extracted to solution.
Extraction of hydrogaret mud was 62.1 % of the initial bauxite.
Middle modulus solution conversed by tricalcium hydroaluminate synthesis with Ca(OH)2 according to the equation:

$$Na_2O{\cdot}Al_2O_3 + 3Ca(OH)_2 = 3CAO{\cdot}Al_2O_3{\cdot}6H_2O + 2NaOH \quad (1)$$

The effect of different temperatures from 40 to 100 °C was studied. The optimum conditions for synthesis of tricalcium hydroaluminate were found to be: 100 °C and 3-4 hours. Extraction of Al2O3 into tricalcium hydrogarnet was 64.2-64.6 %, α_k of the obtained solution was 30. Synthesised tricalcium hydroaluminate was analysed to contain 22.3 % Al2O3, 46.6 % CaO.

Tricalcium hydroaluminate decomposition carried out with 3 types of solution:

- alkali solution Na_2O 240 g/L
- sodium-alkali solution Na_2O 120 g/L and Na_2CO_3 20 g/L
- soda solution Na_2CO_3 60-160 g/L

Leaching carried out at 100 °C in temperature-controlled mixer for 180 minutes, and at 180 °C in autoclave for 90 minutes at L:S ratio of 4.

Leaching with sodium-alkali solution proceeds according to the equations:

$$3CaO{\cdot}Al_2O_3{\cdot}6H_2O + 2NaOH = 3Ca(OH)_2 + 2NaAl(OH)_4 \quad (2)$$

$$3CaO{\cdot}Al_2O_3{\cdot}6H_2O + Na_2CO_3 = 3CaCO_3 + 2\,NaAl(OH)_4 \quad (3)$$

$$3CaO{\cdot}Al_2O_3{\cdot}6H_2O + 6Na_2CO_3 + H_2O = 3(CaCO_3{\cdot}NaCO_3{\cdot}2H_2O) + Na_2O{\cdot}Al_2O_3 + 4NaOH + (n+2)H_2O \quad (4)$$

Table 2: Semi - quantitative analysis of tricalcium hydroaluminate leaching sediment at 180 °C

Compound Name	Formula
Calcite, syn	$Ca(CO_3)$
Unnamed_Hydrogarnet, syn	$(CaO)_3(Al_2O_3)_{1.75}(H_2O)_{3.75}$
Sodium Carbonate Oxide	Na_2CO_3

The optimum conditions for decomposition of tricalcium hydroaluminate were found to be: Na_2CO_3 concentration 140-160 g/dm^3, 180 °C. Extraction of Al_2O_3 95-98.3 %. Direct smelting reduction of hydrogarnet mud mixed with charcoal without fluxing additive was studied to selective reduction of iron to obtain steel and slag. It was carried out at 1600-1650 °C at 1 hour.

Amount of charcoal was dosed to charge by on the basis of full reduction of iron oxides by the reactions:

$$Fe_2O_3 + 3C = 2Fe + 3CO \quad (5)$$
$$2Fe_2O_3 + 3C = 4Fe + 3CO_2 \quad (6)$$
$$3Fe_2O_3 + 6C = 6Fe + 3CO + 3CO_2, \quad (7)$$

There are studies on smelting reduction of Bayer red mud to separate iron in pig iron, and aluminium oxide, sodium, and titanium - in slag i.e. if content of iron oxides is 41.95 % in initial mud, for 100 g of mud 6.3 g of charcoal is necessary. Whereas, graphite crucible using, amount of charcoal was 75 % from calculated. 0.5 % of treacle as binding agent was added for dust-priming decreasing. It was briquetting at a pressure of 200 kg /cm^2, then dried in drying furnace at 350-400 °C for moisture

removal, which was added with treacle liquid. Obtained briquettes was strong enough.

Extraction ratio of pig iron was 35.0 % and slag was 37.5 %. Slag determined to contain 94.7 % Fe, 3.2 % Si, 1.8 % Ti, 0.52 % Al, 0.001 % P, 2.2 % C, 0.38 % Cr, 0.101 % Mn, 0.043 % Ni, 0.052 % Cu. Slag was divided into magnetic and nonmagnetic factions after magnetic separation. As a result 34.5 % magnetic and 66.0 % nonmagnetic factions separated.

Magnetic faction determined to contain 8.24 % Al_2O_3, 14.57 % SiO_2, 16.13 % CaO, 37.56 % Fe, 23.5 % TiO_2. Nonmagnetic faction determined to contain 23.48 % Al_2O_3, 20.3 % SiO_2, 50.32 % CaO, 0.22 % Fe, 1.78 % TiO_2.

Extraction of iron in pig iron was 88.0 %, in magnetic faction – 11.9 % and in nonmagnetic faction – 0.1 %.

Table 3: Magnetic faction of slag

Compound Name	Formula
Suessite	$(Fe_3Si)_{0.5}$
Wustite, syn	$Fe_{0.942}$ O
Hongquiite, syn (NR)	$(TiO_{1.27})_{0.787}$
Iron	Fe
Aluminium Oxide	Al O
Quartz low, syn	SiO_2
Gehlenite, syn	Ca_2Al_2 SiO_7
Andradite	$Ca_3Fe_{1.88}(SiO_4)_3$

Table 4: Nonmagnetic faction of slag

Compound Name	Formula
Calcio-olivine, syn	Ca_2SiO_4
Calcium Oxide	CaO
Gehlenite	Ca_2Al_2 SiO_7
Aluminium Titanium	$AlTi_3$
Calcium Oxide	CaO_2

Table 5: The phase composition of pig iron

Compound Name	Formula
Iron	Fe
Iron Silicon	$Fe_{0.9}Si_{0.1}$
Moissanite-69R	SiC
Gupeiite, syn	Fe_3Si
Graphite	C

Conclusions

As a result of processing of red mud by hydrogarnet technology alkali regenerated into alkali-aluminate solution for 98.0 %, Al_2O_3 extraction ratio was 64.9 % and hydrogarnet mud –silicaferrous concentrate with high consumer properties.
The optimum conditions for synthesis of tricalcium hydroaluminate were found to be: 100 °C and 3-4 hours. Extraction of Al_2O_3 into tricalcium hydrogarnet was 64.2-64.6 %, α_k of the obtained solution was 30.

The optimum conditions for decomposition of tricalcium hydroaluminate were found to be: Na_2CO_3 concentration 140-160 g/l, 180 °C and 2 hours. Extraction rate of Al_2O_3 was 95-98.3 %.

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