HCl-BENEFICIATION OF BAUXITES FOR THE MANUFACTURE OF REFRACTORIES

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In ladle degassing, ex-furnace processing, and vacuum treatment of steel from the ladle using DH and RH methods, linings made from high-alumina refractories are used since these make it possible to achieve a low oxygen concentration in the steel, to facilitate desulfuration, and also to effect other metallurgical processes which improve the quality of the metal.

For the lining of the ladles in ferrous metallurgy, the capitalist countries make the most use of Guyanan and Chinese bauxites with a mass concentration of 86-88% of Al_2O_3 and 2.0-2.5% of Fe_2O_3. In the U.S.A., 900,000 tons of Guyanan bauxite are used annually plus 2,500,000 tons from the State of Georgia. As a result of the development of high-quality steel-smelting, refractory production in Denmark makes use of refractories made from Surinam bauxites. The raw bauxite is crushed, homogenized in relation to fractions, and fired at 1750°C in rotary furnaces of diameter 3 and length 100 m [1, 2].

In the present paper we report some results of a study of the properties of a bauxite concentrate and of the refractories based on it. The concentrate is obtained from standard bauxite and is of interest as a raw material for refractories. The average chemical composition of the bauxite is given in Table 1.

Standard bauxite is currently used in the production of alumina, and the low-iron variety for the production of refractories [3, 4].

The mineral composition of the experimental bauxite is boehmite (34.5%), gibbsite (14.0%), kaolinite (38.5%), hematite (7.2%), anatase and rutile (2.8%), and gypsum (1.2%).

It is clear from Table 1 that the standard bauxite contains an average amount of iron, titanium, and calcium oxides. The refractoriness of the bauxite is 1530-1580°C.

Because of the scarcity of refractory raw materials, there is considerable interest in the beneficiation of bauxites, which can be done using the following methods: leaching by means of acids, selective chlorination, reducing-fusion in electric-arc furnaces, physical methods such as flotation, magnetic separation, and separation by color and, of course, by a combination of the above methods [5].

To obtain a bauxite concentrate, more complex methods are proposed, for example, a reducing and acid method developed by the All-Union Institute of the Aluminum, Magnesium, and Electrode Industry and the All-Union Institute of Refractories. This method includes the reducing-firing of bauxite in a carbon-containing material at 1000-1350°C followed by treatment in acid and ending with the firing of the concentrate in an oxidizing medium at 1350-1650°C.

In the reducing-firing, the compounds of iron are mainly reduced to the metallic state and after the acid treatment (H_2SO_4 or HCl) they are transferred into the solution and partly enter the glass phase; during firing the Al_2O_3 changes to α-corundum and mullite and as a result is not removed by the acid. The material obtained contains no kaolinite and is easily filtered.

The above institutes have now developed a simpler method of HCl beneficiation of bauxite. The layout of this system is shown in Fig. 1. The HCl beneficiation is based on the solubility in hot HCl of ferrous and other impurities contained in the kaolinite and boehmite in the form of solid solutions [6-8]. The solid residue obtained as a result of the acid leaching and washing is the bauxite concentrate.

All-Union Institute of Refractories. All-Union Institute of the Aluminum, Magnesium, and Electrode Industry. Translated from Ogneupory, No. 10, pp. 24-29, October, 1984.

TABLE 1. Chemical Composition of the Bauxites

Bauxite	Mass fraction, %								
	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	TiO_2	Cr_2O_3	S	$\Delta m_{l.o.i}$
Standard	53,6	18,2	7,2	0,7	0,2	2,8	0,6	0,3	16,4
Low-iron									
I	55,9	18,8	2,8	1,3	Not det'd.	3,5	0,64	0,1	15,9
II	52,7—56,1	18,6—20,1	3,2—5,1	0,8—1,7	0,2	3,0—3,6	Not det'd.	1,9—2,5	13,5—17,6
III	48,8	19,6	4,6	0,9	Not det'd.	1,9	Not det'd.		23,7

TABLE 2. Composition of Bauxite and Concentrates

Material	Leaching temp., °C	Mass fraction of oxides for sintering material, %											$\Delta m_{l.o.i}$, %
		Al_2O_3	SiO_2	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	FeO	Cr_2O_3	P_2O_5	
Original bauxite . .	—	61,3	24,1	4,10	8,30	1,10	0,20	0,50	0,05	0,10	0,6	0,15	14,00
Raw bauxite concentrate	75	68,8	27,2	1,00	0,84	0,98	0,14	0,25	0,12	0,74		0,56	16,21
The same	110	66,8	29,1	1,10	0,56	1,10	0,14	0,24	0,12	0,50		0,81	14,38
Bauxite concentrate fired at 700°C	110	48,5	48,4	1,02	1,00	0,60	0,40	0,08	0,06	—	—	—	15,40

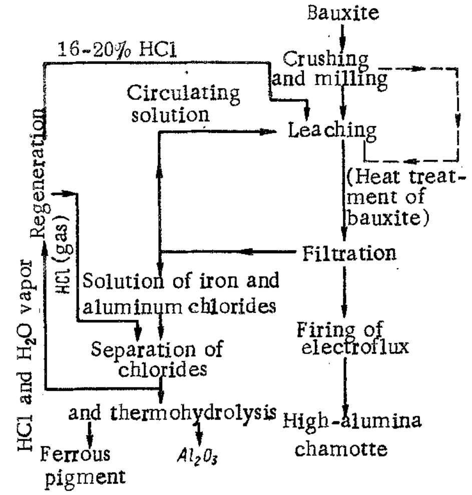

Fig. 1. Layout of system for the HCl beneficiation of bauxite.

The fluxes, Fe_2O_3, Al_2O_3, MgO, CaO, and TiO_2, pass into the chloride solution. As a result of the lower solubility of aluminum chloride, the $AlCl_3 \cdot 6H_2O$ can be separated from the chloride mixture in order to obtain by separate thermohydrolysis technical alumina, the raw material for high-alumina and corundum refractories for the ex-furnace treatment of steel; these refractories are mainly manufactured from alumina. The gaseous products of the thermohydrolysis of iron and aluminum chlorides are returned to the process in the form of an acid and dry HCl for the concentration of aluminum chloride.

The acid beneficiation of ferrous bauxites, unlike the processes which are the basis of alumina production (Bayer method and sintering), is a waste-free process since under thermohydrolysis a ferrous pigment is obtained from the iron chlorides. By changing the temperature of the heat treatment it is possible to regulate the depth of extraction, thus making it possible to produce refractories with different concentrations of alumina.

The composition of the bauxite used for the laboratory studies is given in Table 2.

The concentrate was obtained in two stages: the first stage was the leaching in circulating solution and the second, leaching in 20% HCl. The liquid:solid ratio (liq:sol) after leaching in both stages is 2:1. The slurry obtained in a threefold washing in water at 95°C for 30 min is liq:sol = 3:1.

TABLE 3. Extraction of Oxides When Bauxite Is Leached in the Circulating Solutions at 75°C (numerator) and 110°C (denominator)

Leaching process	Concn. in soln.,* g/liter			Volume of solution, ml		Concn. of oxides in soln., g	
	Al_2O_3	Fe_2O_3	Cl^-	before leaching	after leaching	Al_2O_3	Fe_2O_3
First stage (circulating solution)	31,12/45,80	33,80/34,48	211,19/212,47	100/100	71/85	0,24/1,93	1,28/2,15
Second stage (20% HCl)	11,22/26,26	14,14/11,14	198,7/209,9	—	60/50	0,67/1,31	0,85/0,56
Washing	1,76/1,32	1,04/0,58	15,47/18,34	—	360/400	0,63/0,53	0,37/0,23
Total extract	—	—	—	—	—	1,54/3,77	2,50/2,94

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*Results of quantitative analysis.

TABLE 4. Extraction of Oxides When Raw Bauxite (numerator) and Bauxite Fired at 700°C (denominator) Are Leached in 20% HCl

Leaching process	Concn. in solution,* g/liter			Vol. of solution, ml	Concn. of oxides in solution, g	
	Al_2O_3	Fe_2O_3	Cl		Al_2O_3	Fe_2O_3
First stage . . .	19,4/110,9	18,5/24,5	236,0/240,5	130/90	2,52/9,08	2,41/2,21
Second stage . . .	27,2/78,0	2.86/8,59	211,6/218,8	90/85	2.46/6,63	0,26/0,73
Washing	1,1/7,2	1,00/0,43	14,6/19,6	410/380	0,48/2,74	0,41/0,16
Total extract	—	—	—	—	5.45/18,45	3,08/3,10

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*Results of quantitative analysis.

TABLE 5. Composition of Batches

Batch No.	Mass fraction of components, %		
	bauxite concentrate	α-alumina	by-product alumina
1	100	—	—
2	75	25	—
3	50	50	—
4	25	75	—
5	—	—	100

TABLE 6. Properties of Fired Specimens*

Batch No.	Concn. of Al_2O_3, %	Linear shrinkage, %	Apparent density, g/cm³	True density, g/cm³	Open porosity, %	Water absorption, %	Melting point, °C
1	66,90	16/17	2,3/2,1	3,08/3,08	10,2/6,9	4,5/3,3	1850±20
2	74,46	14/15	2,1/2,2	3,21/3,22	20,0/15,8	9,7/7,0	1980±30
3	82,80	15/15	2,1/2,4	3,41/3,46	21,7/22,2	10,2/9,0	1990±30
4	91,40	15/16	2,4/2,6	3,68/3,66	21,0/21,5	8,4/8,2	1950±30
5	98,30	—/17	—/1,4	—	—/49,1	—/31,5	2000±30

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*Numerator gives values for firing at 1600°C; denominator, at 1700°C.

TABLE 7. Phase Composition of the Specimens

Batch No.	Firing temp., °C	Concn., %			Basicity of mullite, %	Concn of glass phase, %	Comp. of glass phase, %				Comp. of insoluble residue, %			
		corundum in insoluble residue	in mullite Al_2O_3	in mullite SiO_2			SiO_2	Al_2O_3	Fe_2O_3	other oxides	SiO_2	TiO_2	Al_2O_3	Fe_2O_3
1	1600	2,41	70,98	23,80	1,75	16,09	58,05	32,41	1,12	8,39	23,86	1,10	73,39	0,81
	1700	5,52	69,70	22,85	1,79	16,05	61,43	23,99	2,12	12,46	22,95	1,12	75,22	0,57
2	1600	20,07	59,90	18,29	1,97	11,80	51,86	32,80	0,51	14,83	18,29	0,94	79,37	0,64
	1700	20,83	59,29	18,00	1,93	11,34	52,65	30,69	0,44	16,22	18,00	0,36	80,12	0,64
3	1600	53,37	35,40	10,00	2,06	11,54	50,35	37,69	0,78	11,18	10,00	0,64	88,77	0,42
	1700	52,23	36,49	10,00	2,11	9,06	63,90	22,08	2,22	13,80	10,00	0,60	88,72	0,41
4	1600	84,00	11,81	3,75	2,00	7,19	47,29	34,63	0,89	17,39	3,85	0,40	95,81	0,21
	1700	82,15	13,55	3,75	2,17	6,89	50,94	33,38	0,15	15,53	3,75	0,42	95,70	0,21

In the first stage of the study we tried leaching regimes at 75 and 110°C. A 50-g portion of fractions <0.5 mm of raw bauxite was placed in a flask with a ground glass stopper; the flask was filled with the circulating solution so that the composition of the solution remained constant relative to the concentration of Al_2O_3 and Fe_2O_3. On the basis of the probable reactions which occur on beneficiation, we calculated the composition of the circulating solution and in the first stage of leaching used a solution containing 19.66 g/liter of Al_2O_3, 11.22 g/liter of Fe_2O_3, and 215.22 g/liter of Cl.

Both stages of leaching were carried out over 2.5-4 h with continuous agitation of the pulp. After each stage of leaching the solution was separated from the residue by filtration and the concentration of Al_2O_3, Fe_2O_3, and Cl determined.

Table 3 gives the data on the extraction of oxides when bauxite is leached at 75 and 110°C.

It is clear from Tables 2 and 3 that when raw bauxite is leached in two stages at 75 and 110°C it is possible to obtain a concentrate with a low concentration of iron oxides of up to 2%. The extraction of the oxides is as follows, %: titanium, 70 and 70; iron, 79 and 88; and aluminum, 6 and 14.

It must be pointed out that P_2O_5 is also present in the concentrate. When the leaching temperature is increased from 75 to 110°C, the extraction of iron oxide is increased from 79.5 to 85% and that of aluminum increases threefold.

The following stage in the experimental studies was to investigate the leaching of raw bauxite which had been fired in advance at 700°C. The temperature of 700°C was chosen for the preliminary firing after taking into account the thermal behavior of the bauxite minerals, boehmite, gibbsite, and kaolinite, which between 400 and 600°C undergo dehydration and structural transformations which facilitate the significant extraction of alumina. In order to simplify the work and to obtain maximum leaching, we used 20% HCl instead of the circulating solution; in both stages of leaching the liq:sol ratio was 3:1.

The results of the studies are shown in Table 4. When the raw bauxite is treated in HCl, the extraction of alumina is higher (20%) than when leaching takes place in the circulating solution. Even more Al_2O_3 is extracted from bauxite which has been fired at 700°C (71%). This concentrate with a low concentration of alumina (48%) can be used in the production of high-alumina ladle refractories as manufactured from the Arkalyks clays. Firing at 700°C is also reasonable where it is necessary to produce alumina for other types of refractory production, for example, for articles with a concentration of alumina higher than in the original bauxite or the concentrate.

To study the properties of the alumina produced in stages, we used a saturated solution of $AlCl_3 \cdot 6H_2O$. The solution of density 2.9 g/cm^3 was evaporated and the evaporated residue was separated from the mother solution by filtration and calcined at 600°C for 2 h.

To evaluate the properties of the material obtained we determined the pouring mass (0.38 g/cm^3), the true density (2.70 g/cm^3) and the specific surface (45,900 m^2/g); we studied the IR spectra and carried out a differential thermal analysis.

There is a well-expressed exothermal effect at 810°C with a mass loss of 2.20% on the DTA pattern. It is possible that this characterizes the transition of the amorphous form to γ-Al_2O_3. The IR transmission spectrum of a sample of material is characterized by a single broad, diffuse band in the 400-1000-cm^{-1} interval unlike the IR spectrum of corundum in which in approximately the same interval there is a series of bands including some characteristic narrow bands (485, 435, and 380 cm^{-1}) and a poorly resolved wide band with a minimum at 650 cm^{-1}. The IR spectrum obtained cannot be ascribed with any certainty to γ-alumina.

There are a few intense lines of the low-temperature form of γ-alumina on the x-ray pattern of the tested sample but even the most intense line is quite weak and on this basis we can assume that there is a significant amount of amorphous alumina in the sample. If that assumption is true then it is more probable that the spectrum obtained is characteristic of the amorphous component.

Taking into account that the density of γ-alumina is 3.29-3.42 and of amorphous alumina 1.65-1.69 while the true density of the material obtained is 2.70 g/cm^3, we can assume that this material is a mixture of γ- and amorphous alumina.

The following materials were used to obtain a high-alumina chamotte: bauxite concentrate obtained by acid beneficiation at 105-110°C;

to obtain this, we milled the bauxite on a roller crusher to fractions of <1 mm, treated it in a 20% solution of HCl in a water bath in the liq:sol ratio of 2.5:1 for 2 h; the HCl solution was decanted and the concentrate twice washed in hot water in the liq:sol ratio of 3:1 in a porcelain tank; the washed concentrate was transferred to aluminum dishes and dried at 100°C; the chemical composition of the concentrate was as follows, %: Al_2O_3, 67.0; SiO_2, 29.04; TiO_2, 0.87; Fe_2O_3, 0.82; CaO, 0.38; MgO, 0.33; K_2O, 0.35; and Na_2O, 0.48:

α-alumina, hammered in a laboratory vibromill for 0.5 h with a material:ball ratio of 1:4;

alumina (γ- and amorphous forms), obtained from $AlCl_3 \cdot 6H_2O$ using the process described above (by-product alumina).

The compositions of the batches are shown in Table 5.

Assuming that the bauxite concentrate has low plasticity (5-7 in accordance with GOST 5184-64) the batches when mixed were wetted with a solution of sulfite distillery waste at a density of 1.2 g/cm^3. The amount of sulfite distillery waste solution was $\leqslant$ 10% of the mass of the batch.

Cylinders of diameter 36 and height 40 mm were pressed at 70 MPa from the masses obtained. The cylinders were fired in a batch furnace on saggars with a corundum fill. The firing was done at 1600 and 1700°C with an isothermal dwell for 1 h at the maximum temperature; the rate of increase in temperature was 50°C/h. The specimens of batch No. 5 were fired only at 1700°C.

The properties of the fired specimens are given in Table 6. An increase in the firing temperature from 1600 to 1700°C has virtually no effect on the properties of the specimens. Firing at these temperatures is sufficient for the sintering of the concentrate but does not ensure the sintering of the materials with an addition of alumina. This refers entirely to specimens of the by-product alumina, which at the chosen firing temperatures are virtually unsintered and have a water absorption of 30%.

The melting point of the specimens is fairly high and increases with the concentration of Al_2O_3.

The specimens were subjected to a combined chemical analysis during which their chemical composition, the value and composition of the insoluble residue, and the concentration of corundum were all determined.

To determine the value of the insoluble residue, a sample was treated in a mixture of 20% HF and 15% HCl (1:1) for 15 min in cold with the aim of dissolving the glass phase; the insoluble residue was a mixture of mullite and corundum.

In parallel we determined the concentration of corundum in the insoluble residue. For this purpose we dissolved a portion of the residue in a 36-38% solution of HF and heated the mixture for 30 min in a water bath. In this case the glass phase and mullite were virtually completely dissolved but the corundum remained in the residue. The residue was washed with water and then boiled in 8% H_2SO_4 in order to remove the silicon fluoride. The residue then obtained (corundum) was filtered off, calcined, and weighed. The results of the chemical analysis are given in Table 7.

The microscopic study of the insoluble residues showed that they contain no glass phase but consist of mullite and corundum. This made it possible to calculate the basicity of the mullite and the composition of the glass phase in the specimens (Table 7).

We may conclude that the specimens made from the concentrate contain an insignificant concentration of corundum and 80-82% of mullite; with an increase in the firing temperature, the concentration of corundum in the specimens increases. With an increase in the concentration of alumina, the composition of the mullite approaches that of $2Al_2O_3 \cdot SiO_2$ while in the specimens from the concentrate it is intermediate between mullite and pragite. The Al_2O_3/SiO_2 ratio is 1.75-1.79.

The concentration of glass phase is maximal in the specimens based on concentrate and is lower when the concentration of alumina is increased.

It must be emphasized that an increase in the firing temperature from 1600 to 1700°C is not significantly reflected in the phase composition of the specimens.

The results obtained suggest that the bauxite concentrate and the by-product alumina are suitable in chemical composition for the manufacture of aluminosilicate refractories of mullite—silica and mullite—corundum compositions.

The by-product alumina at 1600-1700°C can be used as a lightweight refractory material or as a slag neutralizer for equipment of portion-by-portion vacuum treatment of steel.

It must be pointed out that it was not possible to obtain a dense high-alumina chamotte by firing from a mixture of concentrate and α-Al_2O_3. Therefore, to obtain a filler we used the method of electrosmelting a mixture of concentrate plus 7% of the by-product alumina.

The phase composition of the molten material was predominantly mullite, glass phase, and corundum (respectively, 76.6, 13.4, and 9.96%). The characteristics of the refractory made from the fused material are as follows: mass fraction of Al_2O_3, 72%: ultimate compressive strength, 72-76 MPa; apparent density, 2.67 g/cm^3; open porosity, 21-23%; temperature of onset of deformation under a load of 0.2 MPa, 1690°C; and thermal-shock resistance (1300°C — water), 26 heat cycles.

The promising nature of this bauxite raw material for the production of refractories for the vacuum treatment and ex-furnace processing of steel was shown by the experience of the Borovich Refractory Combine, which successfully produced ladle equipment with the addition of 40% chamotte from low-iron varieties of bauxite. These articles were successfully tested at the Cherepovetsk Metallurgical Combine in a UVS-130 [4]. Moreover, the low-iron bauxites and the concentrate are necessary in the production of refractories for rotary cement furnaces and in the alumina industry.

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