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CHLORIDIZING ALUMINA-CONTAINING ORE

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ABSTRACT OF THE DISCLOSURE

A method of beneficiating or upgrading alumina-silica or aluminum-silicate ores, especially natural clays containing substantial amounts of minerals such as kyanite, diaspore and the like, wherein the ore is heated to a relatively high temperature and treated with chlorine.

BACKGROUND OF THE INVENTION

The present invention is in the broad field of metallurgy and in particular non-ferrous metallurgy. The invention especially relates to the beneficiation or chemical treatment of alumina-silica or aluminum-silicate ores and/or ores containing compounds of both aluminum and silicon for production of concentrates for electrothermal or carbothermic manufacture of aluminum-silicon alloys.

Natural aluminum-silicate ores, especially clays such as those largely comprising diaspore, kyanite, or the like contain large amounts of aluminum in oxidic form and also contain substantial quantities of iron and titanium generally in oxidic form although sometimes as sulfides or other entities. In the production of aluminum-silicon alloys from these high aluminum bearing ores, the iron and titanium metals produced by coreduction with the aluminum and silicon are harmful impurities.

It has been found [N. I. Eremin, A. S. Bessonova, and V. G. Brin, Tr. Vses. Alyumin-Magnievo Inst., 62 (1968)] that chlorination of kaolin and other types of alkali-free alumino-silicate raw materials is the most effective method for production of concentrates for electrothermal manufacture of aluminum-silicon alloys. Heating of the kaolin to 700–1300° C. followed by passage of chlorine is recommended by Takamura Suzuki in Japanese Pat. No. 135-(54), Feb. 11, 1954.

A method of removing iron by heating kaolins with carbonaceous materials in a current of chlorine was proposed by M. E. Nordberg in U.S. Pat. No. 2,141,444 issued Dec. 27, 1938. The possibility of volatilization of iron compounds from kaolins by means of chlorine was noted by T. Haase, Silikattechnik, 9 (1952), and by means of hydrogen chloride by V. I. Spitsyn, Chlorination of Oxides and Nitric Compounds (in Russian) (1931).

Kaolin minerals include kaolinite, dickite, nacrite, onauxite and halloysite-endellite. These minerals contain quantities of aluminum and silicon usually in the form of Al_2O_3 and SiO_2, respectively or as compounds thereof. Such compounds may be $(Al_2O_3)_x \cdot (SiO_2)_y \cdot {}_zH_2O$, where x, y and z are normally small whole numbers such as 0, 1, 2, 3, etc. The alumina seldom exceeds 40% and generally ranges from about 32% to about 39% of the kaolin. Silica generally comprises about 40% to about 53%. Iron in the form of Fe_2O_3 and occasionally FeO comprises less than 2% of the kaolin and usually only about 0.3% to about 1.7%. Titanium (TiO_2) content ranges up to about 3% from a low of about 0.2%. Kaolin thus contains relatively small amounts of iron and titanium and even smaller amounts of alkali metals and chlorination has been reported to have achieved some reductions of these impurities in these relatively pure compounds. The process is not known to have been used commercially.

High-alumina clay minerals such as diaspore, and the like, although containing over 50% alumina, contain substantially larger amounts of compounds containing iron and titanium, frequently about 8% and 6%, when calculated as Fe_2O_3 and TiO_2, respectively, or even higher in some cases. In order for such a mineral or natural ore to be used in the manufacture of aluminum-silicon alloys, the iron and titanium content must be substantially reduced, and ideally to something less than 1% of the ore on the same basis.

It is therefore a primary object of the present invention to provide a means for beneficiating or upgrading natural ores containing large amounts of alumina, smaller amounts of silica and substantial amounts of undesirable compounds of iron and titanium, usually in the form of oxides.

Another object of the present invention is to reduce the iron and titanium content of diaspore clay by treating such clay with chlorine at temperatures of from about 900° C. to about 1200° C.

Other objects and advantages of the present invention will become readily apparent from the hereinafter description of the invention.

SUMMARY OF THE INVENTION

It has been unexpectedly discovered that aluminosilicate ores or natural clays containing large quantities of alumina, i.e., at least about 50% alumina by weight of calcined ore or on a water-free basis, and substantial quantities of both iron and titanium can be beneficiated and/or their iron and titanium contents substantially reduced by treating the ore or clay with chlorine, preferably in the form of a gas at temperatures ranging from about 900° C. to about 1200° C. Higher temperatures up to that at which Al_2O_3 or SiO_2 is unduly attacked may be used, but little additional reduction of impurities is obtained.

Optimum results are obtained at temperatures of from about 950° C. to about 1100° C.

Although the present invention is particularly directed to those natural clays containing substantial quantities of diaspore or kyanite minerals, other alumina-silica ores of high alumina content may be used. Some examples of other minerals are sillimanite, andalusite, mullite, nepheline, pyrophyllite, gibbsite, boehmite and cliachite. Diaspore clay comprises chiefly diaspore and boehmite, both $Al_2O_3 \cdot H_2O$.

Although the clay may be heated prior to being contacted with the chlorine gas, it is preferred that the heating and chlorination occur simultaneously.

In the preferred form of the invention, the ore is precrushed to the required mesh size. A mesh size of about —50 mesh (U.S. Sieve Series) or smaller is essential to effective titanium and iron removal. Smaller mesh sizes produce optimum results.

Little or no reduction of iron and titanium is obtained when bromine and iodine are used in lieu of chlorine. Fluorine has detrimental or deleterious effects on the ore and is undesirable.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In the preferred form of the invention, diaspore clay of relatively fine mesh (about —400 mesh to about —50 mesh, U.S. Sieve Series) is placed in a suitable reactor in a furnace and heated to a temperature in excess of 900° C. and preferably to about 950–1100° C. While heating, a stream of chlorine gas is introduced into the reactor through a suitable opening therein, in such fashion as to provide intimate contact with the previously charged hot finely divided diaspore clay, and the volatile products of reaction plus any excess chlorine passed therethrough and

passed out a second opening in the reactor. The clay is treated or chlorinated for a period of time which will vary depending upon temperature, particle size of the clay, amount of iron and titanium present in the clay, degree of reduction in iron and titanium content desired and rate of chlorine flow, but is conveniently and frequently about two to four hours. Relatively large titanium containing ores require longer heating periods, about 2 to 4 hours. The residual ore is then ready for the next processing step.

A number of laboratory tests have been made wherein various sizes and types of clay minerals were treated with chlorine. The results of these tests are set forth hereinafter.

GENERAL PROCEDURE

(1) The mineral was placed in a ceramic boat and the boat was placed in a high temperature glass or ceramic tube. The tube was inserted in a tube furnace and heated to the desired temperature. The temperature was measured using a Chromel-Alumel thermocouple inside a Vycor protection tube with the end of the protection tube located over the boat. A stream of chlorine was passed through the tube, over the boat and out the other end of the tube. After the test the residual ore was cooled and weighed. Extractions were calculated by determining weight of each material in the feed and in the product.

(2) The mineral was placed in a vertical Vycor tube with a Vycor frit near the bottom. The tube was inserted in a vertical furnace. A stream of inert gas, usually argon, was passed through the bed to fluidize it. Temperature was measured with a Chrome-Alumel thermocouple encased in a Vycor protection tube inserted down the reaction tube with the end of the protection tube below the top of the bed of mineral. After the desired temperature was attained, the inert gas was shut off and chlorine or a mixture of chlorine and inert gas was turned on. At the end of the test, the reactor was cooled and the results calculated as in the foregoing paragraph 1.

The temperature may be measured by any convenient method. The tube may be of high temperature glass, ceramic or other material. In lieu of the fritted disc, any other suitable means for producing increased uniformity of gas flow in the horizontal periphery may be used. In addition to argon, nitrogen, helium or other similar inert gases may be employed.

Chlorine and/or the mixture of chlorine and inert gas is passed through the ore at a sufficient rate to form a fluidized bed.

Example I

Following General Procedure 1, small amounts of diaspore of −400 mesh were placed in a boat and treated with chlorine at elevated temperatures. Tests were run at 500°, 700° and 900° C. Iron and titanium removal was in excess of 90%. All calculations on extraction are based on weight of feed x fraction of component in feed and weight of product x fraction of component in product. The results are set forth in Table 1 hereinafter.

TABLE 1

	Percent feed	Analyses, percent			Extractions, percent		
		500° C.	700° C.	900° C.	500° C.	700° C.	900° C.
Al_2O_3	56.2	67.5	69.8	76.3	+2.8	0.2	2.5
SiO_2	10.8	13.5	13.8	15.8	+7.0	+2.8	5.1
Fe_2O_3	8.2	6.9	2.6	1.2	28.0	74.4	89.5
TiO_2	5.4	6.3	6.4	0.8	0.4	5.1	89.2

Example II

Following General Procedure 1, a sample of −325 mesh kyanite concentrate was chlorinated at 900° C. The results are as follows:

TABLE 2

	Percent		
	Starting material	Product	Extraction
Al_2O_3	53.2	53.2	2.86
SiO_2	43.8	44.4	1.54
Fe_2O_3	1.5	0.3	80.51
TiO_2	1.6	0.2	88.10

Example III

Following General Procedure 1 or 2, samples of kyanite and diaspore of various sizes were tested at several temperatures in horizontal boats and in a vertical tube. The results of these tests are set forth in Table 3 as follows:

TABLE 3

Temp., ° C.	Percent			
	Al_2O_3	SiO_2	Fe_2O_3	TiO_2
Tests in horizontal boats—General Procedure 1				
−400 mesh diaspore:				
Starting ore	56.2	10.8	8.2	5.4
500	67.5	13.5	6.9	6.3
700	69.8	13.8	2.6	6.4
900	76.3	15.8	1.2	0.8
900	73.4	15.8	1.4	0.8
100/150 mesh diaspore:				
Starting ore	64.0	5.8	9.7	3.7
1000	82.2	6.2	1.4	0.9
−325 mesh kyanite:				
Starting ore	53.2	43.8	1.5	1.6
900	53.2	44.4	0.3	0.2
1000	52.3	41.6	0.15	0.65
Tests in vertical tube—General Procedure 2				
−400 mesh diaspore:				
Starting ore	56.2	10.8	8.2	5.4
800	58.7	15.4	3.0	6.0
1000	75.1	14.0	1.0	0.7
100/150 mesh diaspore:				
Starting ore	64.0	5.8	9.7	3.7
800	81.5	5.6	1.4	3.1
−325 mesh kyanite:				
Starting ore	53.2	43.8	1.5	1.6
800	51.2	40.4	0.3	1.6

Although iron can be removed at 800° C., titanium removal is ineffective.

Example IV

Following General Procedure 2, samples of 30 grams each of 100/150 mesh diaspore clay were treated with pure chlorine at 1000° C. for 3¾ hours. The results are as follows:

TABLE 4

	Starting ore, percent	1000° C., Cl_2, 225 min.	
		Analysis, percent	Extraction, percent
Al_2O_3	55.6	67.1	8.8
SiO_2	10.6	12.8	8.8
Fe_2O_3	5.7	0.6	91.8
TiO_2	4.8	0.8	87.5

Example V

Using General Procedure 2, fluidized bed tests were run on a number of 30 gram samples of 100/150 mesh diaspore clay at temperatures of 900° C. and 1000° C. for various lengths of time using pure chlorine and a mixture of chlorine and argon (40–45% Cl_2 by volume). Analysis of the diaspore was Al_2O_3—56.5%, SiO_2—11.1%, Fe_2O_3—5.7%, and TiO_2—4.7%. The results were as follows:

TABLE 5

Temp., ° C.	Gas used	Time, hrs.	Analysis, percent	
			Fe_2O_3	TiO_2
1000	Cl_2	3.75	0.6	0.8
1000	Cl_2	3.75	1.0	2.1
1000	Cl_2	2	0.9	2.5
1000	Cl_2+Ar	3.75	0.7	3.4
900	Cl_2	2	1.7	4.4
900	Cl_2+Ar	2	0.8	3.9

Example VI

Using General Procedure 1, samples of 200/325 mesh diaspore ore were treated with chlorine at temperatures of 900° C. and 1000° C. for one hour and two hours. The results of these tests are recorded hereinafter in Table 6.

TABLE 6

Chlorination of 200/325 mesh ore at 900° C.

Constituent	Starting ore, percent	1 hour Composition, percent	1 hour Extraction, percent	2 hours Composition, percent	2 hours Extraction, percent
Al_2O_3	58.70	70.6	6.4	74.9	5.8
SiO_2	12.25	13.5	14.4	14.3	13.9
Fe_2O_3	7.10	1.6	82.6	1.4	85.5
TiO_2	4.45	5.0	12.7	3.4	44.0

Chlorination of 200/325 mesh ore at 1000° C.

Constituent	1 hour Composition, percent	1 hour Extraction, percent	2 hours 1st test Composition, percent	2 hours 1st test Extraction, percent	2 hours 2nd test Composition, percent	2 hours 2nd test Extraction, percent
Al_2O_3	73.0	4.4	75.4	8.2	78.5	3.8
SiO_2	15.7	1.6	14.5	15.5	14.7	13.9
Fe_2O_3	0.9	90.1	1.2	87.8	0.8	92.0
TiO_2	3.9	32.8	1.8	70.9	0.8	87.3

From the foregoing data it can readily be seen that the chlorination of natural ores such as kyanite and diaspore substantially reduces the iron and titanium impurities in such ores and makes them suitable for further processing, especially the manufacture of aluminum-silicon alloys.

Other impurities occurring in natural ores, such as vanadium, chromium, nickel, manganese, sodium, potassium, calcium and magnesium, although generally occurring in considerably less amounts than iron and titanium, may also be reduced by the method of the present invention.

The present invention provides a relatively simple method for effectively simultaneously reducing the iron and titanium content of alumina-silica ores to be subsequently carbothermically reduced or otherwise reduced for making aluminum-silicon alloys. If such ores did not contain titanium, they could be treated by physical beneficiation means which would usually be sufficient for iron reduction.

Although lower temperatures can be employed in reducing the iron content of the natural ore or clay, a temperature of at least about 900° C. is essential for titanium reduction.

The present invention provides a means for making titanium tetrachloride ($TiCl_4$) as the titanium tetrachloride is formed during chlorination of the ore at 900° C. or above is volatized and may be collected in any suitable manner.

The foregoing disclosure and description of the invention is illustrative and explanatory thereof and various changes in the treating procedure may be made within the scope of the appended claims without departing from the spirit of the invention.

What is claimed is:

1. A method of simultaneously reducing the titanium and iron content of an alumina-silica ore or clay containing at least about 50% alumina by weight on a water-free basis and substantial amounts of iron and titanium compounds, comprising the steps of fluidizing particles consisting essentially of such ore or clay and smaller than 50 mesh U.S. Sieve Series at a temperature of between about 950 and 1200° C. by means of a stream consisting essentially of chlorine sufficient to react with and remove most of the iron and titanium from the particles.

2. The combination of claim **1** in which the particles are diaspore and have a size no larger than 100 mesh U.S. Sieve Series, and the treating temperature is between about 950 and 1100° C.

3. The combination of claim **2** in which the particles are no larger than 400 mesh U.S. Sieve Series.

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