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The waste reduction technology of chloride contaminated red-mud from by-product of Bayer process

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Abstract: The general red-mud minerals consist of hematite, sodalite, anatase, quartz, gibbsite and miner impurities. This gives serious environmental damage for the ocean disposal. It mixed with chloride compound and the content of chlorine is about 2,000-3,000ppm.This paper can be suggested the chloride reduction technology that is applied basically mineral processing by physical separation. Then it can be possible to produce the totally 24wt. % useful red-mud which chloride content is less then 400ppm.

1. Introduction

The alumina is one of the important materials of refractory industry and ceramic fields that can use alumina as polishing material, engineering ceramics and the source of inorganic raw materials. Most of the alumina products came from the Bayer process. That process discharged a much amount of solid waste called red-mud in the precipitated zone. This discharged red-mud is very fine size distribution and main components are silica, hematite, sodalite, calcium, anatase and miner impurities. The color likes red-brick to iron-oxidation. The character of red-mud is very high alkali state (pH 10-12.5) cause by sodium-hydroxide treatment for the extraction of alumina and its solid pulp density is about 15-30wt. % as in-situ state. The general red-mud mixed with chloride compound and the content of chlorine is about 2,000-3,000ppm. Therefore it is different to us for the recycling such as auxiliary raw material of cement industry and etc. And most of red-mud is ocean disposal without any treatment for the extraction of harmful materials as chloride compound. For that reason, it is big problem to solve how to control of environmental damage and protection of the law of international regulations. The regulation permitted below the 500ppm of chlorine content in the chloride compound. This paper can be suggested the chloride reduction technology that is applied basically mineral processing by physical separation.

2. Sample & Experimental methods

The red-mud samples were supplied from Japanese company. Table 1. shown that chemical compositions of red-mud head sample.

Table 1. Chemical compositions of red-mud head sample using XRF.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Cl
wt. %	8.4	0.6	18.7	13.8	0.4	0.3	1.9	7.3	0.5	48.1	0.23

Generally, the red-mud takes chemical compound of Fe_2O_3, Al_2O_3, SiO_2, Na_2O and Cl as 48.1wt.%, 18.7wt.%, 13.8wt.%, 8.4wt.% and 0.23wt.%, respectively. The red-mud consisted of various kinds of minerals and the shape of particles is different for their own property. Especially, it is high pulp density and mixed with aggregated hematite materials. For that reason, we would classify red-mud by wet-sieve first and divided into 4 fractions such as below 44 ㎛, 44 ㎛-74 ㎛, 74 ㎛-149 ㎛ and over 149 ㎛ by JIS standard. The fraction of below 44 ㎛ takes more detailed classification by Cyclosizer consisting of five cyclones.

That general process is shown in Fig. 1.

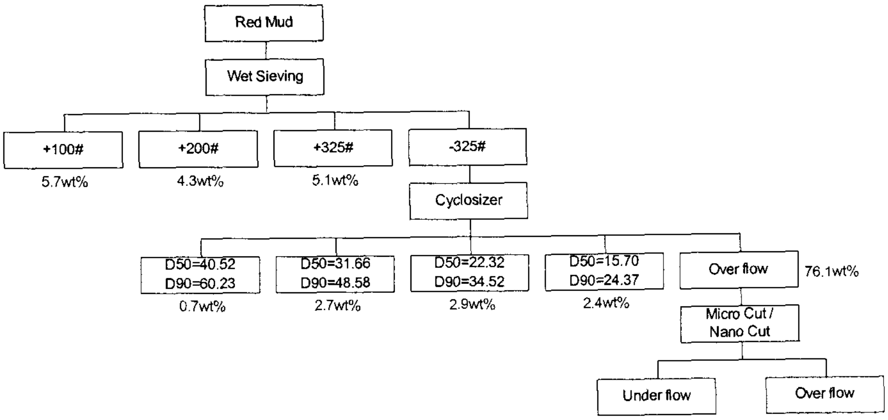

Fig. 1. The flow sheet of mineral processing by physical treatment with the red-mud.

The physico-chemical properties of the separated red-mud were investigated by using XRF(X-ray fluorescence analysis, JSX-321, JEOL, Japan), XRD(X-ray diffraction analysis,RINT-2000, Regaku Japan), SEM(Scanning Electron Microscope ; JSW-5410, JEOL, Japan) and EDS (Energy Dispersive Spectroscope ; JED-2100, JEOL, Japan).The size distribution and size classifications are used particle size analyzer (Sympatec Helos & Pods, sucell, Germany) and Cyclosizer(Warman International LTD, Austlalia).

3. Results and discussion

The sample's solid pulp density is approximately 60wt. %. That can be dried about 24 hours at 105℃ and takes chemical analysis as shown in Table 1.

Table 1 shows that 4 major elements, consist with 5 miner elements are impurities. And content of chloride is 2300ppm. It seems like similar phenomena compare to the by-products of Bayer process.[1] Especially, in case of hematite contents is 48.1% that is the other value-added material for recycling.

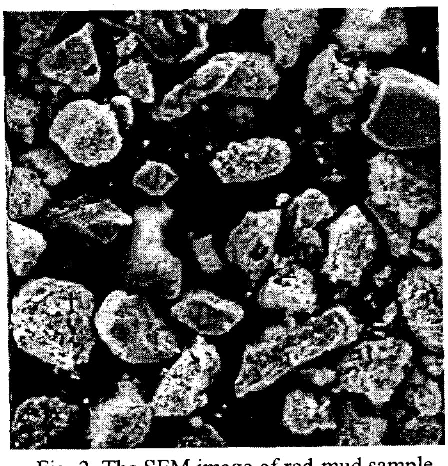

Fig. 2. The SEM image of red-mud sample.

Fig.2 shows that SEM image of red-mud head sample. We observed various kinds of shape and size samples. It seems complicated mineralogical compound and various minerals existed. That reason, we would classify red-mud by wet-sieve first.

Table 2. Chemical compositions of each products separated by wet sieving (unit: wt. %).

㎛	Wt %	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Cl
+ 149 ㎛	5.7	3.4	0.1	21.4	12.1	0.1	0.1	1.5	2.3	0.5	58.4	0.06
74 ㎛- 149 ㎛	4.3	2.2	0.1	19.2	8.6	0.3	0.0	3.6	5.4	0.6	60.0	0.00
44 ㎛- 74 ㎛	5.1	2.1	0.3	16.6	6.1	0.4	0.0	5.4	6.9	0.6	61.5	0.00
-44 ㎛	84.9	9.4	0.7	18.7	14.5	0.4	0.2	1.6	7.7	0.5	46.1	0.27

Table 2. shows that the 84.9wt. % of red-mud(below 44 ㎛) is consist of very fine particle and contents of chloride is about 2700ppm. The 15.1 wt. % of red-mud (over 44 ㎛) obtained chloride less than 300ppm and the content of iron is about 60wt. % determined. From this wet sieving results shows that it is easily obtain the suitable materials with a chloride less than 300ppm products by sieving method first.

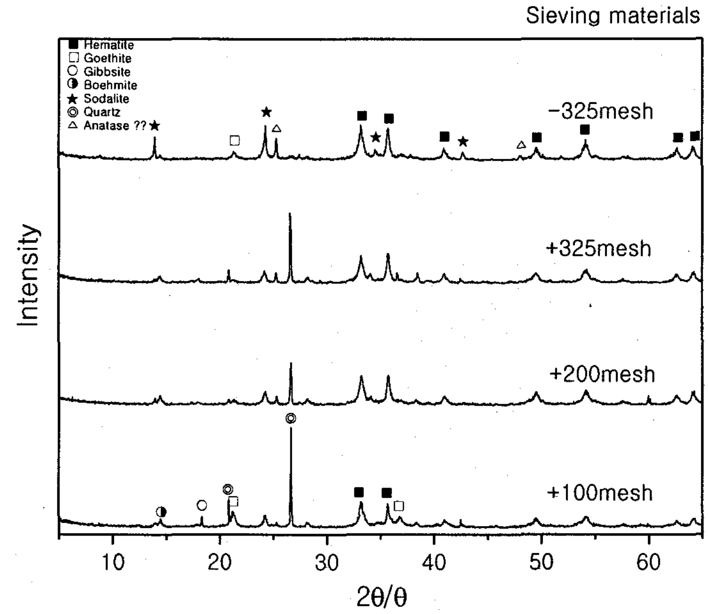

Fig. 3. XRD pattern of each products separated by wet sieving.

Fig. 3 shows that over 44 ㎛ samples mainly consisted of quartz, hematite and gibbsite, on the other hand below 44 ㎛ samples consisted sodalite and hematite. Our test result that the fraction of 44 ㎛ under size particles were about 85wt. % with the head sample of red-mud. It means that we need the more detailed treatment to reduce under 44 ㎛ sample amount by using physical separation. Under 44 ㎛ sample can be implemented for detailed size fraction using Cyclosizer.

As shown in Fig.3, under 44 ㎛ sample is consisted with sodalite, hematite and ilmenite. These minerals produced precipitated by-products during the sodium-hydroxide treatment for the extraction of alumina from the Byer process. At this process can be appears precipitated synthetic materials which kaolinite reaction with bauxite impurities named sodalite-type desilication product (DSP = $Na_6[AlSiO_4]_6 \cdot 2NaX \cdot nH_2O \rightarrow X = ½CO_3^{2-}, ½SO_4^{2-}, Cl^-, OH^-$)[2]. And accompanied minerals are Goetite($FeO(OH)$), Anatase(TiO_2), Gibbsite($Al(OH)_3$), Rutile/Anatase(TiO_2) and Calcite($CaCO_3$) as a XRD analysis.

It can be seems that the waste reduction of chloride compound is physical separation first then chemical and solidification method is followed. This treatment process is economical process for the treatment of chloride compound from the red-mud. Table 2 shows that under 44 ㎛ products are about 85wt. % produced and divided more detailed size fractions for the contents of chloride compound contained fine size.We take multi-gravity separation for the economical cutting point using Cyclosizer with 5 stage cyclone. Table 3. shows that size distribution of fine particle using cyclosizer and their chemical compositions.

Table 3. Chemical compositions of each fraction separated by cyclosizer (unit: wt%).

㎛	Wt (%)	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Cl
D_{50}=40.52	1.0	1.3	0.3	13.4	6.4	0.6	0.1	2.7	9.2	0.1	65.8	0.00
D_{50}=31.66	3.2	1.8	0.4	13.6	5.9	0.6	0.1	4.9	8.1	0.1	64.5	0.04
D_{50}=22.32	3.4	2.0	0.4	13.7	5.9	0.6	0.1	4.1	8.6	0.1	64.5	0.02
D_{50}=15.70	2.8	2.6	0.4	13.4	6.0	0.6	0.2	3.0	9.1	0.2	64.4	0.03
Over Flow	89.6	10.2	0.7	19.3	15.5	0.4	0.2	1.3	7.5	0.6	44.0	0.30

Table 3. shows that the 89.6wt. % of red-mud (overflow) is consist of very fine particle and contents of chloride is about 3,000ppm. The 10.4 wt. % of red-mud (over 15.7 ㎛) obtained chloride less than 400ppm and the content of iron is about 65wt. % determined.

The red-mud sample(overflow) takes chemical compound of Fe_2O_3, Al_2O_3, SiO_2 and Na_2O as 44wt.%, 19.3wt.%, 15.5wt.% and 10.2wt.%, respectively. And the red-mud sample(over 15.7 ㎛) takes average chemical compound of Fe_2O_3, Al_2O_3, SiO_2 and Na_2O as 65wt.%, 13wt.%, 6wt.% and 2wt.%, respectively.

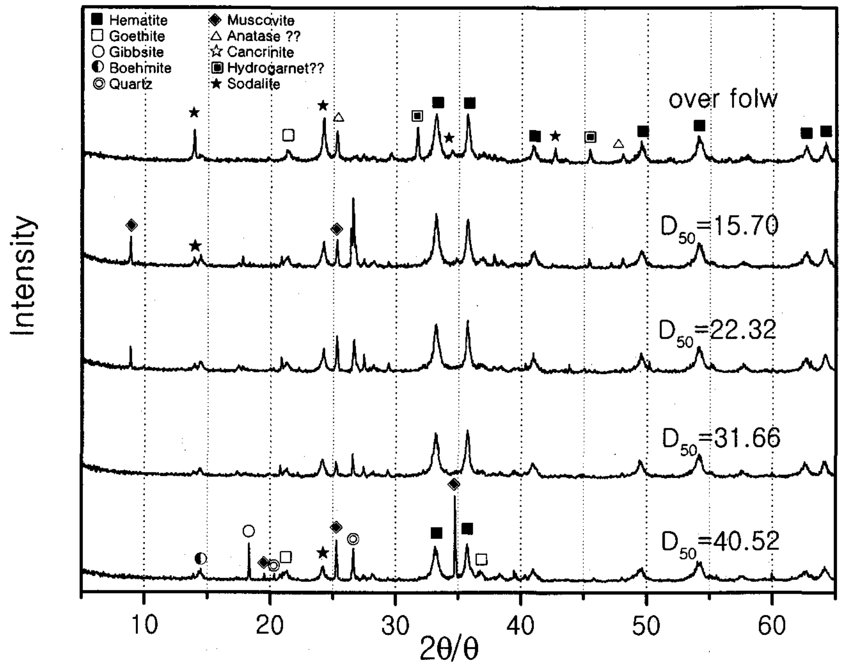

Fig. 4. XRD pattern of each products separated by cyclosizer.

Fig. 4 shows that under 44 ㎛ particles were divided into 5 kinds of products by cyclocizer. In case of below 15 ㎛ products took a chloride elements about 3,000ppm and yield is about 90%. And the other fractions contained such as over 15.7 ㎛ products less than 400ppm chloride elements.

4. Conclusions

We studied the reduction ratio of chloride compound of red-mud from the alumina industry by Bayer-process using physical separation technology.

a. By sieving test, over 44 ㎛ particles are control of the chloride compound less then 300ppm and it is 15.2wt. %

b. Under 44 ㎛ particles are separated into finer fractions by cyclocyzer. The recovery of useful red-mud of low chloride content is 10.4wt. % around over 15.7 ㎛. And chloride content is less than 400ppm.

c. Thus, it can be possible to produce the totally 24wt. % useful red-mud whose chloride content is less than 400ppm by physical separation technology.

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