Note

Identification of Magnesium Oxides

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Introduction

Magnesium oxides may be divided into three types according to the manufacturing method and the properties.

A) Fused magnesia

B) Sintered magnesia (Dead-burned magnesia)

C) Light-burned magnesia (Caustic-burned magnesia)

In addition, there are two different products in each of three types. The one is from magnesite and the other is from sea water.

Fused magnesia is manufactured by fusion of sintered magnesia in an electric furnace at above 2,800 ℃ ,and then by cooling to crystallize magnesium oxide. The content of magnesium oxide is very high, generally over 98%.It has excellent properties for heat resistance, electric resistance and optics, so it is used for ceramics, insulating material, optical elements, etc.

Sintered magnesia is manufactured by calcining magnesite or magnesium hydroxide precipitated by addition of calcium hydroxide to sea water. The calcining temperature is over 900℃,generally 1,500 ～2,000℃.The product from magnesite contains 90～95% of magnesium oxide. The one from sea water usually contains over 95% of magnesium oxide.

Sintered magnesia is used for refractory of blast furnace or refractory bricks. The output now is the most abundance compared with other two types.

Light-burned magnesia is manufactured by calcining magnesium hydroxide from sea water or magnesite at 900℃ or less. But nowadays the production from sea water is most common. It is characteristic in chemical activity compared with other two types. It is used for pharmaceutical material, industrial chemicals as a filler for rubber, paper and cosmetics or chemical reagent.

In the present Customs Tariff Schedules, it is necessary to identify the above mentioned three types and/or the origin whether from magnesite or sea water, at the classification of magnesium oxides.

It is considered that there must be any differences in physical and chemical properties among those products.

Previously we reported [1] on the identification between sintered magnesia from magnesite and from sea water. Now following examination was carried out to identify them.

Experimental

Samples

Samples used for the examination were 14—fused magnesia 3,sintered magnesia 6,light burned magnesia 5,as shown in Table 1.

Sample No.2,3,4,5,6,7 and 9 were crushed into fine powder to pass a 250 mesh sieve. Other samples No.1,8,10,11,12,13 and 14 were directly employed to the following examination, since these were fine enough to pass a 250 mesh sieve.

Appearance

Shape and colour were observed on the samples.

Moisture(JIS K 6224 method) [2]

Weigh 2g of sample into a glass lidded weighing bottle, put it in an electric constant air bath for 2 hrs. at 105～110℃.From the difference in weight, moisture was calculated.

Ignition loss(JIS K 6224 method) [2]

Dried sample obtained from above mentioned moisture test was used for the examination.

Weigh 1g of the dried sample into a porcelain

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crucible, put it to get constant weight with an electric furnace at 900°C. From the difference in weight, ignition loss was calculated.

Specific gravity

Air comparison pycnometer method was employed. The atmosphere was replaced with helium to avoid a reaction with oxygen in air.

Apparatus; Beckman-Toshiba air comparison pycnometer, Model 930

Apparent specific gravity(JIS K 6220 method) [3)]

The device consists of a piston and a cylinder made of steel shown in Fig.1.

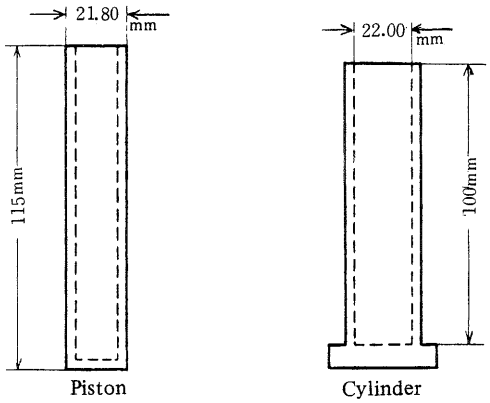

Fig.1 Measuring device for apparent specific gravity

First, put the piston into the cylinder, measure the difference in height between the cylinder top and the piston top. Weigh 2～5g of sample, put it into the cylinder, then the piston is dropped into the cylinder naturally. Again, measure the difference in height between the cylinder top and the piston top. Apparent specific gravity was calculated from the following equation:

$$G = \frac{S}{(H_2 - H_1) \times 0.7854D^2}$$

where G : Apparent specific gravity(g/ml)

S : Weight of sample(g)

H_2 : Difference of the height between the cylinder top and the piston top, when sample was put into(cm)

H_1: Difference of the height between the cylinder top and the piston top, when the cylinder was empty(cm)

D : Diameter of the cylinder(cm)

Electric resistance

Preparation of test piece

Sample was shaped into a disk having 10.5 mm in diameter and 3.1 mm in thickness under high pressure (1 ton/cm²).Heating at 1400°C for an hour, the disk was coated with silver paste on both faces, and again heated to bake the silver paste. The silver acts as electrodes at the measurement of specific electric resistance.

Measurement of specific electric resistance

Specific electric resistance was measured with a high resistance meter (Yokogawa-Hewlett-Packard, Model 4329A) at 100 V on the test piece prepared by the above mentioned method.

At the following three different conditions, the test piece was applied for measurement of specific electric resistance.

Condition A: The test piece, which was left 24 hrs. in contact with air was applied.

Condition B: The test piece which was stored for half an hour in a desiccator filled with silica gel, after drying in an air bath for 4 hrs. at 120°C,was applied.

Condition C: Using the test piece of condition B, the timechange of the value was checked at minutely intervals.

Iodine number

Weigh 1g of sample into a glass stoppered flask, and add 50 ml of 0.1 N I_2 solution. Shaking violently for 30 minutes, filter the sample solution, then take 10 ml aliquots of the filtrate and titrate with 0.05 N sodium thiosulphate solution. Iodine number was calculated from the following equation:

$$I.N. = (V_2 - V_1) \frac{127 \times N_1}{0.2}$$

Table 1 Analytical results of fused, sintered and light-burned magnesia

Note Identification of Magnesium Oxides

Type		Fused			Sintered						Light-burned				
Sample No.		1	2	3	4	5	6	7	8	9	10	11	12	13	14
Produced country		Japan	Japan	Japan	N. Korea	Greece	U. S. S. R.	Japan	Japan	Italy	Japan	Japan	Japan	Japan	Japan
Origin		Sea water	Sea water	Sea water	Magnesite	Magnesite	Magnesite	Sea water	Sea water	Sea water	Sea water	Sea water	Sea water	Sea water	Sea water
Appearance		White fine powder	Granular, Crystal Size: 50-200mesh	Colourless transparent crystal, Size: 3-5mm	Grayish brown lump Size: 3-20mm	White lump Size: 1-10mm	Grayish brown lump Size: 3-20mm	White lump Size: 1-25mm	White fine powder	Pale green lump Size: 5-25mm	White bulky powder	White bulky powder	White bulky powder	White bulky powder	White bulky powder
Moisture (%)		0.23	0.24	0.28	0.48	0.31	0.29	0.13	0.31	0.38	0.77	0.83	0.64	1.19	0.80
Ignition loss (%)		0.06	0.09	0.11	1.21	1.31	1.62	0.49	1.31	0.39	3.43	3.79	3.27	4.45	5.76
Specific gravity		3.59	3.59	3.56	3.25	3.29	3.25	3.15	3.25	3.22	3.32	3.23	3.32	3.20	3.00
Apparent specific gravity		1.38	1.39	1.35	1.01	1.22	1.40	1.24	1.22	1.13	0.45	0.28	0.34	0.34	0.33
Electric registance (ρ . Ω . cm)		4.6×10^8	—	3.6×10^8	—	—	8.1×10^8	—	—	—	—	—	—	—	—
Iodine number (mg I/g)		0	0	0	0	0	0	0	0	0	23	53	36	82	148
Acid insolubie matter (%)		0	0	0	2.47	0.22	0.69	0.07	0.32	0.85	0	0	0	0	0
MgO (Ignited base) (%)		99.90	99.44	98.75	91.48	96.77	91.00	98.69	94.85	97.11	97.90	97.80	97.40	98.40	98.12
B_2O_3 (ppm)		17	281	357	40	13	23	475	1241	215	1727	1693	2832	3004	1788
Qualitative analysis by * emission spectrography	Mg	+++++	+++++	+++++	+++++	+++++	+++++	+++++	+++++	+++++	+++++	+++++	+++++	+++++	+++++
	Si	+	++	++	++	++	++	++	++	++	++	++	++	++	++
	Ca	+	++	++	+	++	++	+++	++	++	++	++	++	++	++
	Al	tr	–	tr	+	–	tr	tr	tr	tr	tr	tr	tr	tr	tr
	Fe	+	+	+	++	+	++	+	+	++	+	+	+	+	tr
	Cr	tr	tr	tr	tr	tr	+	tr	+	+++	tr	tr	tr	–	–
	B	–	++	++	tr	–	–	++	++	+	++	++	++	++	++

* The symbols marked in this column mean as follows:

+++++ : Very large amount

+++ : Relatively large amount

++ : Small amount

+ : Very small amount

tr : Trace

— : Not detected.

where I.N.: Iodine number(mg I/g)

V_1 : Titer for sample solution(ml)

V_2 : Titer for blank test(ml)

N_1 : Normality of $Na_2S_2O_3$ solution(0.05 ×factor)

Acid insoluble matter (JIS K 6224 method)[2]

Weigh 2g of sample into 500 ml beaker, add 75 ml of water. Stirring it, 25 ml of conc. hydrochloric acid was added and boiled the solution for 5 minutes. Cooling to room temperature, the solution was filtered and washed with hot water. The filter paper with acid insoluble matter was dried and ashed in a porcelain crucible with an electric furnace at 900 ℃. Weighing the residue, acid insoluble matter was calculated.

Magnesium oxide(Method of Japan Society for the Promotion of Science)[1]

EDTA titration method was employed.

Boron oxide

Emission spectrographic method[1) 4)] and method of Japan Society for the Promotion of Science(Alkali titration method)[3)] were employed.

Qualitative analysis

Emission spectrographic method was employed.

Apparatus: Shimadzu plane grating spectrophotograph, Model GE 340

Conditions: DC arc 10 amp,600 lines/mm grating, slit 14 μ,3400 Å center(2200～4600 Å),Fuji process plate

Results and discussion

All the analytical results are shown in Table 1.

Appearance : Fused magnesia is white fine powder or colourless transparent crystal. Sintered magnesia from magnesite is grayish brown or white lump, but from sea water is usually white lump. In some cases it is coloured by some additives. And it is powdered in rare cases. Light-burned magnesia is white bulky powder.

Ignition loss : Fused magnesia is the smallest. Light burned one is the largest. It is the reason why light-burned one usually contains a small amount of magnesium hydroxide or magnesium carbonate, so they are decomposed into magnesium oxide during igniting at 900℃. And the property has relation to iodine number.

Specific gravity : Fused magnesia is the largest. There is not any demarcation line between sintered and lightburned magnesia. The crystal of fused one is large and dense, being understood by the manufacturing process, so it has such a high density.

Apparent specific gravity: Light-burned magnesia is very small. It is caused by the very bulky and porous form.

Electric resistance: Fused magnesia is generally used for electric insulating material, because of having an excellent property of electric insulation. So the electric resistance was measured. The results are shown in Table 2 and 3. But there was no special difference between fused and sintered magnesia as far as the method now performed.

Iodine number: This number is an index to indicate the chemical activity of magnesia. Light-burned magnesia always absorbs iodinate. The number ranges in 23 to 148. This number is concerned with calcining temperature. So the number increases according as getting large of ignition loss.

Table 2 Specific electric resistance of magnesium oxides (condition A and B)

Sample No.		Condition A	Condition B
1	(1)	5.4×10^8 ($\rho.\Omega.$cm)	——
	(2)	4.5×10^8	2.2×10^{11} ($\rho.\Omega.$cm)
	(3)	3.9×10^8	2.3×10^{11}
2	(1)	3.1×10^8	——
	(2)	3.8×10^8	5.3×10^{11}
	(3)	3.8×10^8	5.3×10^{11}
6	(1)	6.2×10^8	——
	(2)	8.7×10^8	5.7×10^{11}
	(3)	9.5×10^8	5.4×10^{11}
8	(1)	6.6×10^8	——
	(2)	7.0×10^8	6.5×10^{11}
	(3)	8.2×10^8	6.2×10^{11}

Table 3 Specific electric resistance of magnesium oxides (condition C)

Time-change	Sample No. 1	Sample No. 8
(min.)	(ρ.Ω.cm)	(ρ.Ω.cm)
0	1.8×10^{11}	6.6×10^{11}
1	8.1×10^{10}	6.3×10^{11}
2	7.0×10^{10}	5.9×10^{11}
3	6.3×10^{10}	5.4×10^{11}
4	6.3×10^{10}	5.3×10^{11}
5	5.4×10^{10}	5.1×10^{11}

Acid insoluble matter: Fused and light-burned magnesia are almost soluble in hydrochloric acid. It is difficult to understand why only in sintered magnesia, acid insoluble matter is appeared. But it could be said that fused magnesia is manufactured by using high grade of sintered magnesia, so it has high purity in magnesium oxide and on one hand lightburned magnesia is very reactive because of being calcined in low temperature.

Boron oxide : All samples from magnesite contain only less than 100 ppm. But magnesia from sea water contains more than 100 ppm except No.1.

Conclusion

Light-burned magnesia is very easy to distinguish from two other types of magnesia with the values of ignition loss, apparent specific gravity and iodine number.

On the identification between fused and sintered magnesia, it is usually distinguishable by appearance, that is, fused magnesia is colourless crystal and sintered one is white or coloured in irregular shape. But in some cases they are fine powder. In the case, ignition loss, specific gravity and magnesium oxide content are deciding factors to distinguish them. Specific gravity of fused magnesia is always over 3.5, and the content of magnesium oxide is very high over 98%. On the identification of the products from magnesite and sea water, the boron oxide content is the best index.

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