

Identification of Seawater Magnesia Clinker and Natural Magnesia Clinker

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For the purpose of identification of seawater magnesia clinker and natural magnesia clinker, qualitative and quantitative analysis and observation of surface profile by scanning electron microscope have been studied on a number of seawater magnesia clinker produced in Japan and natural magnesia clinker imported from North Korea, U.S.S.R and Greece.

Boron content is remarkably different in both of magnesia clinkers, that is, seawater magnesia clinker contains 100 ppm or more of boron oxide, but natural magnesia clinker contains only 40 ppm or less of boron oxide.

And the other difference is that, natural magnesia clinker forms relative large spherical periclase, on the other hand seawater magnesia clinker presents various shapes of periclase and its size is rather smaller than natural magnesia clinker.

So identification of them is possible by applying the above mentioned means.

1. Introduction

Magnesia clinker is a important refractory material used for production of refractory bricks and used as ramming material in steel making furnaces.

There are two types of magnesia clinker. One is obtained from seawater (seawater magnesia clinker), and the other is from magnesite (natural magnesia clinker). Seawater magnesia clinker is manufactured by the following steps. Magnesium ion containing a small amount in seawater is precipitated into magnesium hydroxide with calcium hydroxide. After washing and drying the precipitate, it is calcined into magnesia clinker in a rotary kiln at the temperature of 1,500 to 2,000°C. In this manufacturing process, most cases small amount of silicon oxide, ferric oxide or chromium

oxide, is added into magnesia clinker to obtain a product having a desired thermal property.

Natural magnesia clinker is manufactured by simply calcining magnesite.

It is generally said that seawater magnesia clinker contains 91 to 98% of magnesium oxide and natural magnesia clinker contains 86 to 91% of magnesium oxide¹⁾. However, Greek natural magnesia clinker contains highly of 94% or more of magnesium oxide²⁾.

There is no clear demarcation line between seawater magnesia clinker and natural magnesia clinker on the content of magnesium oxide.

So the following examination has been studied to identify both of magnesia clinkers.

2. Samples

The samples used in the examination are shown in Table 1.

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Table1. Sample of seawater magnesia clinker and natural magnesia clinker

Sample No.	Origin
1	Seawater, produced in Japan
2	" "
3	" "
4	" "
5	" "
6	" "
7	" "
8	" "
9	Magnesite, North Korea
10	" "
11	" Greece
12	" U. S. S. R.

All seawater magnesia clinkers are those produced in Shin Nihon Chemical Industry Co., Ltd. and Ube Chemical Industries Co., Ltd. in Japan. And all natural magnesia clinkers are those imported from North Korea, Greece and U.S.S.R.

3. Experimental

3·1 Qualitative examination

3·1·1 General appearance

Shape and colour were observed on the samples.

3·1·2 Qualitative analysis by emission spectro— photograph

Apparatus; Shimadzu plane grating
spectrophotograph, Model
GE—340

Analytical conditions

Emission; DCA 10 Amp, 20 sec.
Wave length range; 2,400~4,400Å
Slit width; 13 μ
Photo. plate; Fuji spectrographic plate,
Process type
Electrodes; Shimidzu special spectro—
scopic graphite electrodes

Under the above mentioned conditions, powdered samples (see 3.3.1) were analysed.

3·2 Observation of surface profile by scanning electron microscope

Observation results of a fracture of magnesia clinker's periclase by electron microscope have been reported by N.J.Tighe et al³⁾, V. Glibert et al⁴⁾ and T. Ohta¹⁾. They state that periclase profile of fracture remarkably differs in accordance with the compositions of impurities in magnesia clinker.

Now it is considered that there are any differences on the surface profile between seawater magnesia clinker and natural one, because they come from different starting material. The former is magnesium hydroxide precipitated from seawater and the latter is magnesite. And also they have different manufacturing process.

So we observed the surface profile of magnesia clinker using scanning electron microscope.

Apparatus;

- 1) Hitachi scanning electron microscope,
Model MSM—2
- 2) Nihon Denshi scanning electron microscope,
Model JSM—50A

Conditions

Accelerating voltage; 15 KV

Magnification; X 1,000

All samples were coated with carbon and gold.

3·3 Quantitative analysis

3·3·1 Preparation of sample

All samples were pulverized to pass the 250 mesh sieve using Spex mixer mill equipping tungsten carbide capsule.

The fine powdered samples were employed in the above mentioned qualitative analysis (3·1·2) and follow—
ing quantitative analysis.

3·3·2 Measurement of moisture

1 gr. of sample was put in electric air oven at 105 for 1.5 hrs. The heating loss was calculated as moisture.

3·3·3 Measurement of ignition loss and determi— nation of silicon oxide, ferric oxide, alumi— nium oxide, calcium oxide and magnesium oxide

Gakushin method⁵⁾ (The method is offered by Japan Society for the Promotion of Science) was employed in all the following examinations.

The analytical scheme is shown in Fig.1 and the

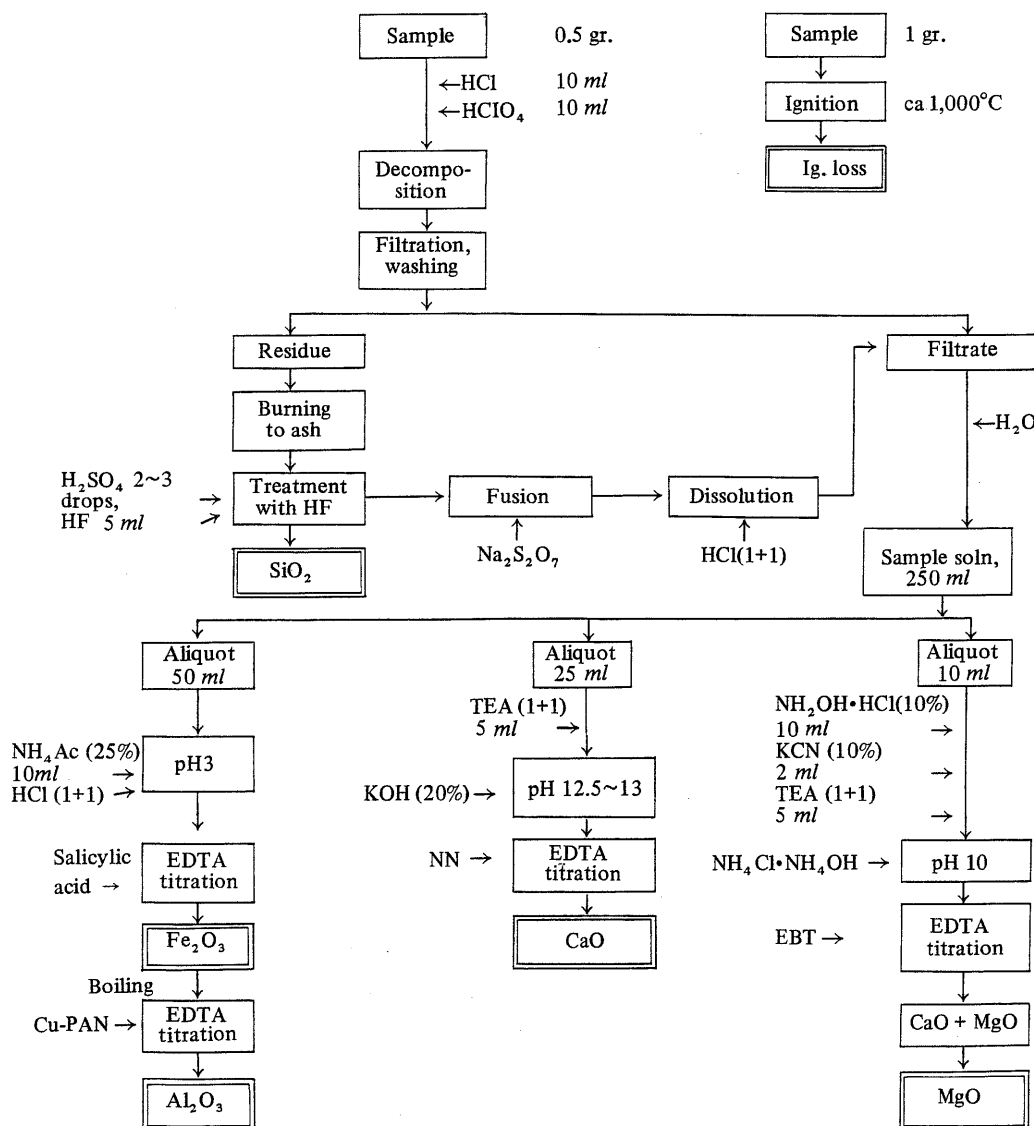


Fig.1 Analytical scheme of Gakushin method for magnesia clinker

summary of the method is as follows;

a) Ignition loss

1 gr. of sample is weighed into platinum crucible, and is ignited in electric furnace at about 1,000°C for 1 hr. The difference of the weight between before and after ignition is calculated as ignition loss.

b) Determination of silicon oxide, ferric oxide, aluminium oxide, calcium oxide and magnesium oxide

0.5 gr. of sample is weighed into a beaker and decomposed with hydrochloric acid and perchloric acid. The decomposed solution is filtrated and washed with water. The residue on the filter paper is burned to ash in a platinum crucible and weighed.

Silicon dioxide in the residue is evaporated by addition of hydrofluoric acid. The difference of the weight between before and after evaporation by hydrofluoric acid is calculated as the content of silicon

dioxide,

The residue treated with hydrofluoric acid is fused with sodium pyrosulfate. The fused salt is dissolved with hydrochloric acid and the solution is mixed together to the solution obtained by filtration of the decomposed solution, and diluted to the mark of 250 ml with water. The mixed solution is employed in following examination.

Ammonium acetate solution is added in 50 ml aliquots of the mixed solution. Adjusting pH to 3 with hydrochloric acid, the solution is titrated with EDTA solution using salicylic acid as indicator. The content of ferric oxide is calculated from the titer.

Successively the solution determined ferric oxide is boiled and titrated at about 80°C with EDTA solution using Cu — PAN as indicator to determine the content of aluminium oxide.

25 ml aliquots of the mixed solution is adjusted pH to 12.5~13.0 with sodium hydroxide solution and is masked interfering substances coexisting in the solution with triethanolamine. Then the solution is titrated with EDTA solution using NN as indicator. The content of calcium oxide is calculated from the titer.

10 ml aliquots of the mixed solution is masked interfering substances coexisting in the solution with masking agent and is adjusted pH to 10 with buffer solution of ammonium chloride plus ammonium hydroxide. Then the solution is titrated with EDTA solution. This titer means the content of calcium oxide and magnesium oxide. So subtracting the calcium oxide content from the total amount, magnesium oxide content is calculated.

3·3·4 Determination of boron

On determination of a small amount of boron in magnesium oxide, ASTM method ⁶⁾, Gakushin method ⁷⁾ and R.M.Dagnall et al ⁸⁾ have been published and reported. But we newly established a emission spectro—photometric method.

Zirconium oxide was used for internal standard, graphite powder and barium fluoride were used as spectro—buffer.

Spectroanalytical lines of 2,496.778 Å and 2,487.288 Å were selected for boron and zirconium respectively.

Apparatus

Emission spectro—

photograph; Shimidzu plane grating spectrograph, Model GE 340

Arc source; Shimidzu ARL modular source, Model 280000

Microphotometer; Shimidzu Model PD 20A

Mixer; Spex mixer mill, No.8000, Plastic vial (50 mm in height, 20 mm in diameter) with three plastic balls

Reagent and others

Zirconium oxide; Nihon Mining Co., Ltd., for nuclear reactor, containing hafnium less than 10 ppm

Graphite powder; Tokai high purity grade spectroscopic graphite, no containing boron

Barium fluoride; Special grade in JIS reagent grade, no containing boron

Carbon electrodes; Tokai high purity grade spectroscopic electrodes

Photo. plate; Kodak spectrum analysis plate No.1 (SA—1)

Developer; D—19

Emission spectroscopic conditions

Emission; DCA 10A

Time of exposure; 30 sec after preburning
60 sec.

Slit width; 16 μ

Gap of electrodes; 4mm

Center of

wave length; 2500 Å, secondary line

Filter; Three steps

Experimental procedure

Preparation of standard sample

Magnesium oxide of no containing boron 1 gr., barium fluoride 0.5 gr., zirconium oxide 0.5 gr. and graphite powder 0.5 gr. were weighed and mixed, then sodium borate aq. solution was added into the mixture respectively to be contained 20, 50, 100, 200 and 500 ppm as B₂O₃. The mixture was dried for 1 hr. in a air

oven at 105°C and thoroughly mixed with Spex mixer mill in a plastic vial.

Analytical sample was prepared as well as standard sample. Then the sample was put in hollow part of graphite electrode by tapping method and emitted.

Developing and drying the photo.plate, the darkness of the spectrum was measured with microphotometer.

The ratio (I_B/I_{Zr}) of darkness (transmittance) of boron to zirconium was plotted on log-log section paper. The analytical working curve is shown in Fig.2. The curve makes a straight line in 20 ppm to 500 ppm.

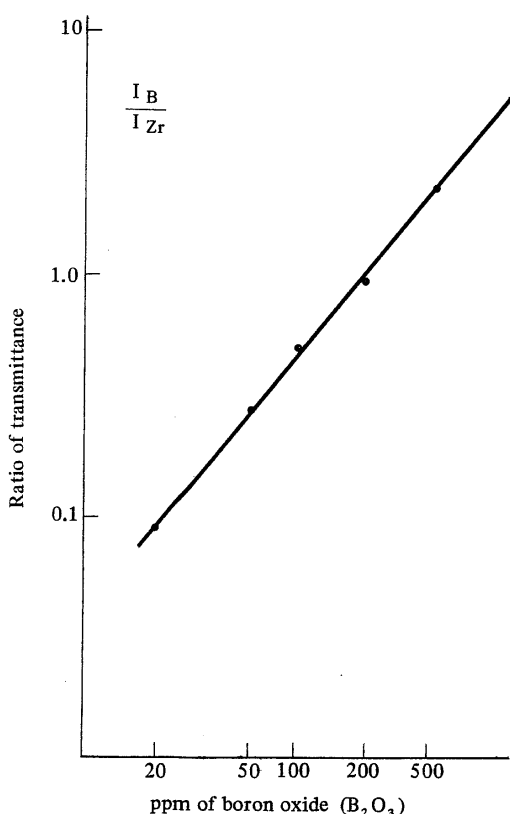


Fig.2 Analytical working curve for magnesia clinker

4. Results and discussion

4.1 General appearance

Observation results of the appearance is summarized in Table 2 and the photographs of some samples are shown in Photo.1 to 8.

Table2 General appearance of magnesia clinker

Sample	Seawater magnesia clinker	Natural magnesia clinker
Appearance		
Shape	Granules, round, powder	Lump, irregular
Colour	White (generally) Brown (Fe_2O_3 added) Greenish white (Cr_2O_3 added) Homogeneous tone	White (Greece) Greyish brown (North Korea, U.S.S.R.) Irregular tone

4.2 Qualitative analysis by emission spectrophotograph

The elements ascertained from the spectra taken by emission spectrophotograph are tabulated in Table 3.

Magnesium, silicon, calcium, iron and aluminium are contained in all samples. Trace of sodium is found in only one sample of natural magnesia clinker and is found in most of seawater magnesia clinker.

Boron is surely found in all seawater magnesia clinker, but it is hardly found in natural magnesia clinker in the above mentioned spectrophotographic conditions (Refer to 3.1.2).

This means that there is a clear difference in boron content between seawater magnesia clinker and natural one. So it is suggested that the identification of both of magnesia clinkers is possible by determination of boron content.

4.3 Observation of surface profile by scanning electron microscope

The photographs of the surface profile taken by scanning electron microscope are shown in Photo.9 to 18.

The periclase in natural magnesia clinker always forms a spherical shape about 10μ to 50μ in diameter resembling potato in shape.

On the other hand, the periclase in seawater magnesia clinker presents various shapes, for example spherical (Photo.15 and 18), scaly form (Photo.13). And the periclase size is very small as compared with natural magnesia clinker.

So there is a clear difference between both of

Table 3 Results of qualitative analysis by emission spectrophotograph

Origin Sample No. Elements	Seawater						Magnesite			
	1	2	3	5	7	8	9	10	11	12
Mg	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
Si	++	++	+	++	++	++	++	++	++	++
Ca	++	++	++	++	++	++	++	++	++	++
Fe	++	++	tr.	tr.	tr.	++	+	+	tr.	+
Al	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.
Na	tr.	tr.	—	tr.	—	tr.	tr.	—	—	—
B	+	+	+	+	+	+	—	—	—	—

+++ ; Very large amount

++ ; Small amount

+ ; Very small amount

tr. ; Trace

— ; No detection

Table 4 Results of determination of magnesia clinker

Origin Sample No. Components	Seawater				Magnesite			
	3	5	7	8	9	10	11	12
Moisture	0.00%	0.08%	0.00%	0.02%	—	0.03%	0.00%	0.02%
Ig. loss	0.50	0.39	0.02	0.24	—	0.50	0.61	0.78
MgO	98.08	94.72	94.90	91.06	91.50%	89.93	95.20	89.26
CaO	0.80	0.95	1.09	2.28	1.11	2.62	2.28	4.44
SiO ₂	0.24	3.04	2.82	1.71	4.85	4.51	1.52	2.64
Fe ₂ O ₃	0.05	0.11	0.09	3.75	1.10	1.20	0.06	1.88
Al ₂ O ₃	0.09	0.50	0.08	0.30	0.23	0.41	0.09	0.65
B ₂ O ₃	0.033	0.300	0.155	0.310	0.004	<0.002	<0.002	<0.002

magnesia clinkers.

Sample No.8 (Photo.18) contains a large amount of ferric oxide. So it is considered that the periclase has been melted in the sintering process of the manufacturing.

Sample No.5 (Photo.15) presents a spherical shape of relatively large size.

Sample No.6 (Photo.16) shows a fracture. This product may have a crushing process in the final stage of the manufacturing. It seems that we could not catch the original surface.

4.4 Quantitative analysis

The results of determination of each sample are

tabulated in Table 4.

Magnesium oxide content in seawater magnesia clinker is generally higher than natural magnesia clinker, and the content of calcium oxide, silicon oxide, ferric oxide and aluminium oxide in seawater magnesia clinker is rather lower than natural magnesia clinker. But on these components there is not any clear demarcation line between both of magnesia clinkers. So it is difficult to identify them by the content of magnesium oxide and the above mentioned impurities.

On the other hand, the content of boron as boron oxide is maximum 40 ppm in natural magnesia clinker, whereas all seawater magnesia clinkers contain 100 ppm or more of boron as boron oxide. So there is a very clear



Photo.1 Natural magnesia clinker
(North Korea)
(Sample No.10)



Photo.2 Natural magnesia clinker
(Greece)
(Sample No.11)



Photo.3 Natural magnesia clinker
(U.S.S.R.)
(Sample No.12)

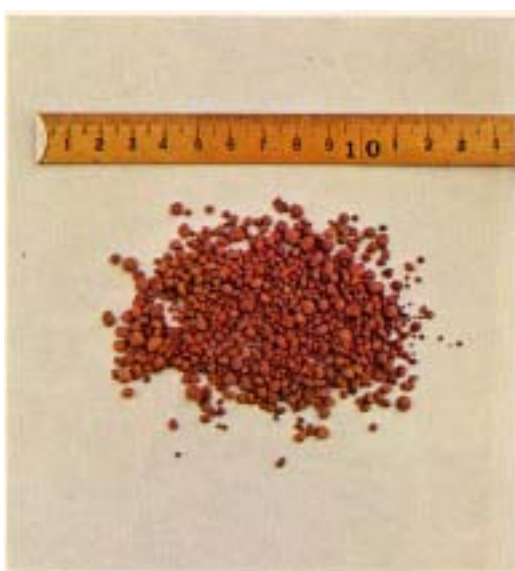


Photo.4 Seawater magnesia clinker
(Sample No.1)



Photo.5 Seawater magnesia clinker
(Sample No.3)



Photo.6 Seawater magnesia clinker
(Sample No.5)



Photo.7 Seawater magnesia clinker
(Sample No.7)



Photo.8 Seawater magnesia clinker
(Sample No.8)

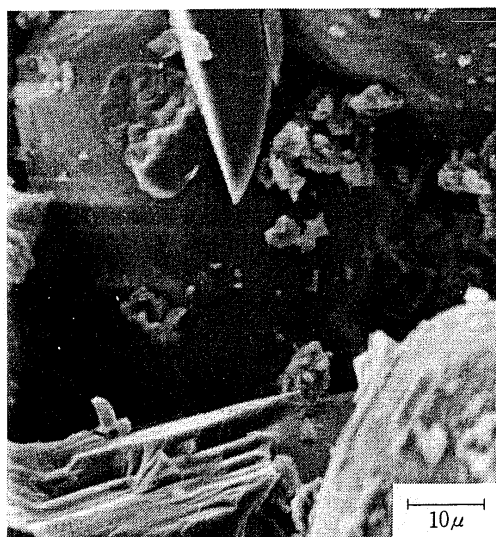


Photo.9 Natural magnesia clinker
(North Korea)
(Sample No.10)

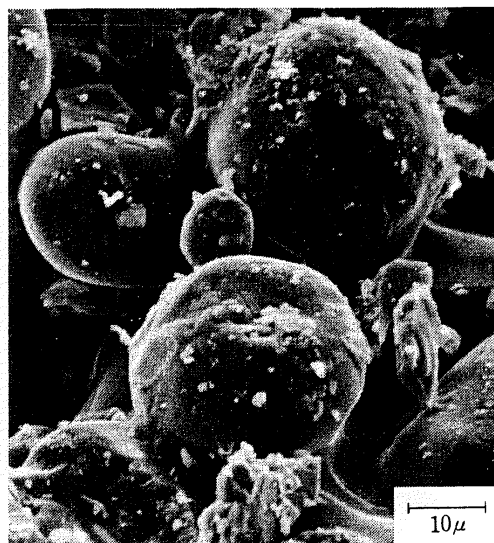


Photo.10 Natural magnesia clinker
(Greece)
(Sample No.11)

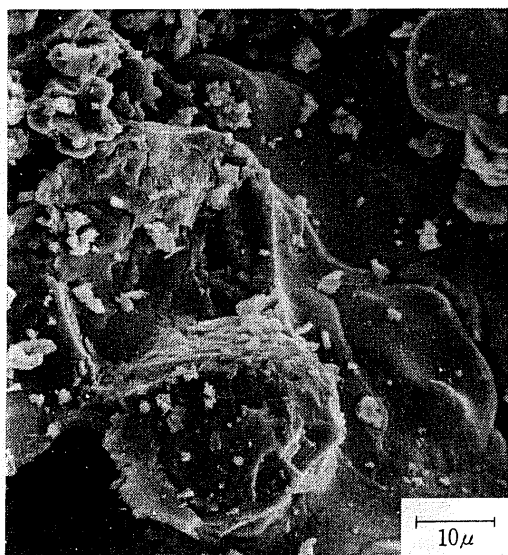


Photo.11 Natural magnesia clinker
(U.S.S.R.)
(Sample.No.12)

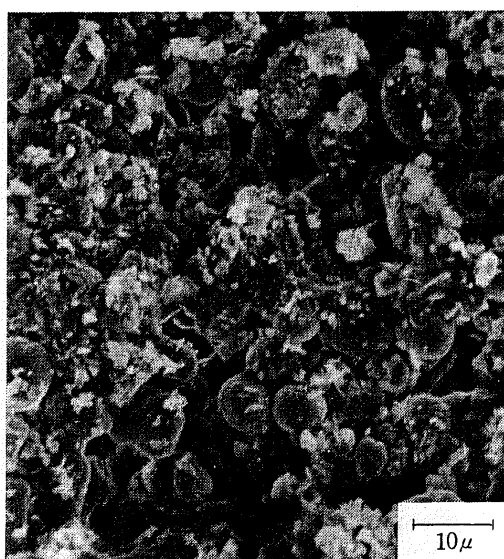


Photo.12 Seawater magnesia clinker
(Sample No.1)

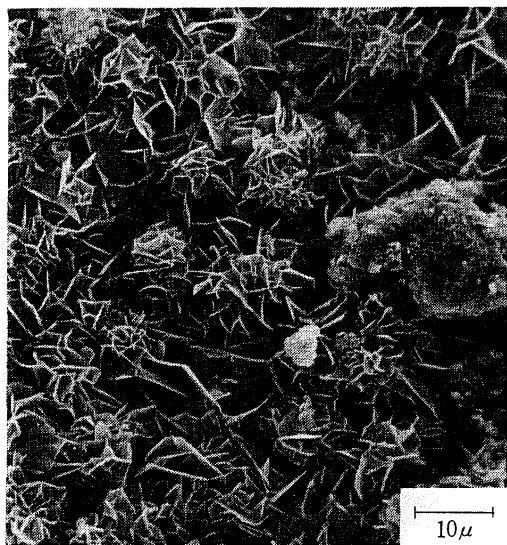


Photo.13 Seawater magnesia clinker
(Sample.No.3)

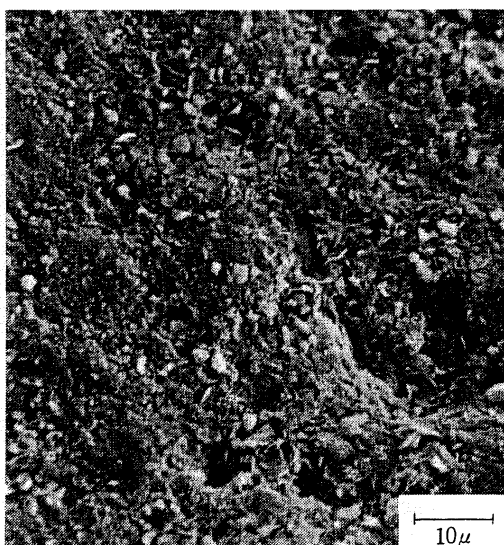


Photo.14 Seawater magnesia clinker
(Sample No.4)

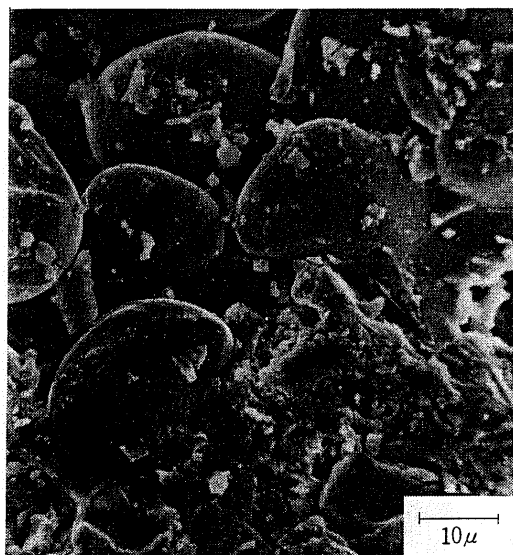


Photo.15 Seawater magnesia clinker
(Sample No.5)

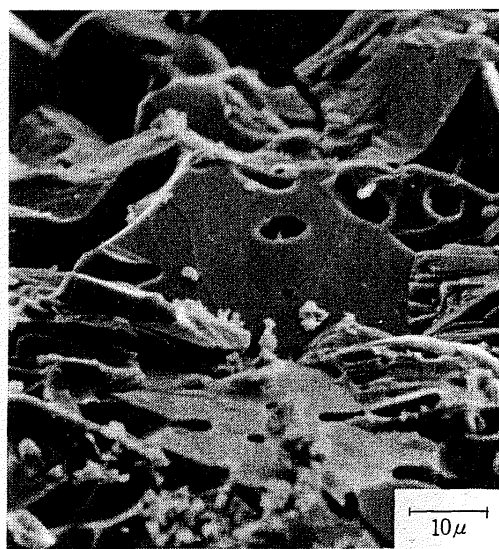


Photo.16 Seawater magnesia clinker
(Sample No.6)

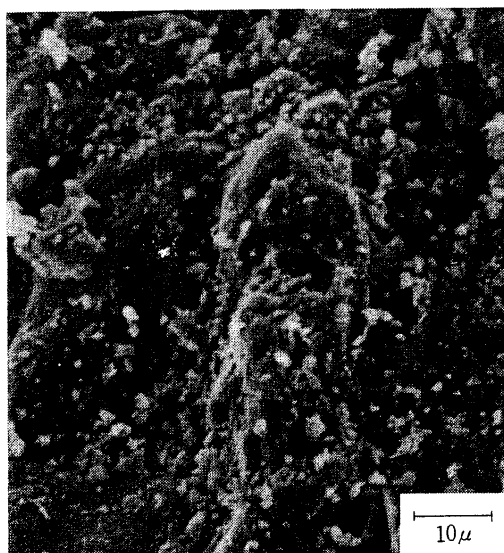


Photo.17 Seawater magnesia clinker
(Sample No.7)

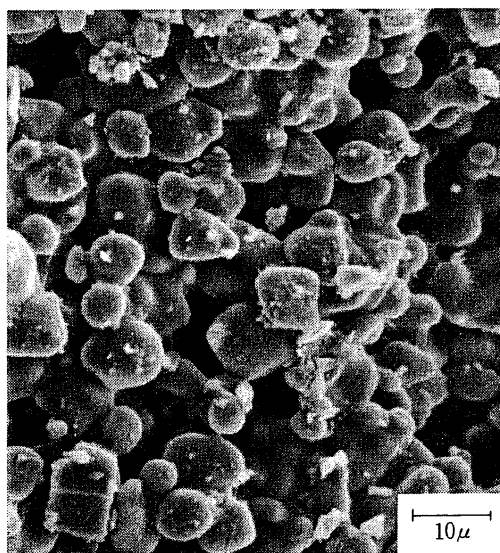


Photo.18 Seawater magnesia clinker
(Sample No.8)

Photo.9~18 photographs of the surface profile of magnesia clinker were taken with scanning electron microscope.

All these photographs were taken by magnification 1,000

difference between them.

Recently decreasing the boron content in seawater magnesia clinker has been technically developing for the purpose of improving the physical property of the clinker, but it is said that lowering the content less than 100 ppm of boron oxide is difficult in view of technical and economical points.

5. Conclusion

Identification of seawater magnesia clinker and natural magnesia clinker is possible by determination of boron, observation of surface profile by scanning electron microscope and of general appearance for example shape and colour.

6. Acknowledgements

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