

XRD and SEM Investigations of KGL, Novel Porous Materials Prepared in the System Chlorite-Sericite-Quartz-Gypsum-Portlandite by Means of Steam Curing

Ko IKEDA*, Chuichi TASHIRO* and Takeshi TOMISAKA**

(Received June 29, 1990)

Abstract

Novel porous materials called KGL have been prepared from mining waste of Kuroko-type ore deposit added with III-anhydrite and portlandite by steam curing. The waste was calcined beforehand up to 1,000°C and then pulverized and screened. The III-anhydrite was prepared from by-product gypsum and slaked lime of chemical was served for portlandite. These three raw materials were mixed in desired proportions and precursors were firstly made by slip cast technique flooded with appropriate amount of water. The precursors were air-dried for several days and then steam-cured for 24 hours. Thus, light weight porous materials have been obtained. The mining waste comprises chlorite, sericite and quartz in addition to some barite. Gypsum and C-S-H were found as hydrates by XRD. SEM observation revealed that acicular to lathlike crystals of gypsum developed mainly, also contributing to the strength development, when calcined the waste at higher temperatures, whereas the gypsum appeared in irregular platy form, when calcined the waste at lower temperatures.

1. Introduction

In the northeastern part of Honshu Island of Japan there are some mines producing Kuroko-type ores, mainly consist of copper, lead and zinc ore minerals. After floatation there remains huge amount of clayey waste containing chlorite, sericite and quartz sometimes associated with barite, pyrite and gypsum.

The annual amount of the waste reaches 120,000 tons in a certain mine and becomes troublesome for mining because of the limitation of discarding dams.

To solve this problem temporary transportation through a pipe line in slurry is being done from the dam site to sea shore to have built an extra dam as illustrated in Fig. 1¹⁾. The pipe line continues approximately 70 km. Therefore, studying utilization of the waste is very benefit not only for mining but also for the conservation of natural environment.

Several attempts have been done hitherto, e.g., production of light weight aggregates for concrete constructions²⁾ and sanitary tiles. Recently we have tried to prepare porous light weight materials called KGL having low thermal conductivity³⁾. In this paper study of hydrates and their textures of KGL will be supplemented intensively by means of XRD and SEM.

* Department of Mining and Mineral Engineering, Yamaguchi University.

**Yamaguchi College, Science University of Tokyo.

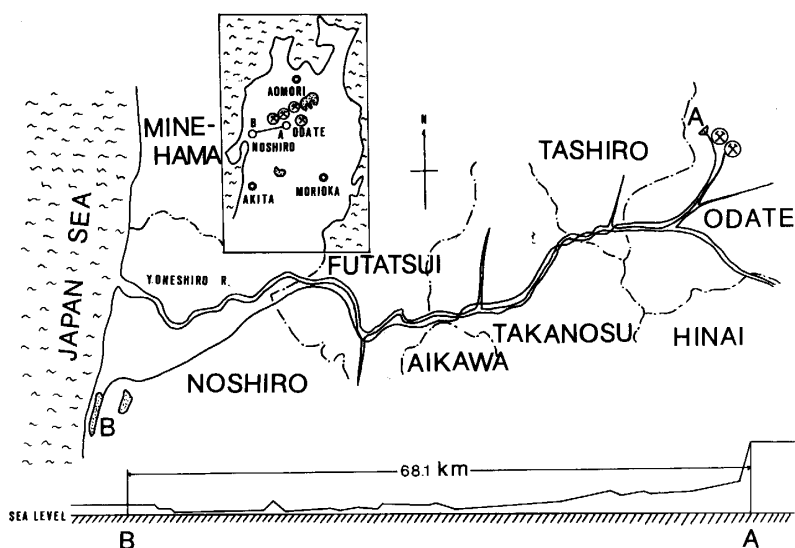


Fig. 1 Route of the pipe line between Odate and Noshiro.

2. Specimens

Production of KGL requires floatation waste, gypsum and portlandite fundamentally in addition to water. Gypsum and portlandite act as activators of pozzolanic reaction. The waste is favorable to be processed at moderately high temperatures beforehand to obtain well-active pozzolanic powder. Following temperatures were selected, 200, 400, 500, 600, 700, 800, 900 and 1,000°C besides R. T., air-dry at room temperature. The duration was 30 minutes* for every specimen but R. T., using 130 cc alumina crucibles. The calcined waste was screened through a 100-mesh sieve after soft grinding in a porcelain mortar.

Gypsum should be converted to III-anhydrite to prepare precursors in a short period of time. Hemihydrate is also will do, but in this study III-anhydrite synthesized from by-product gypsum from a power station was used to heat at 200°C in an oven. Commercially sold JIS first grade chemical was employed for portlandite. The chemical composition of the raw waste is given in Table 1. Physical characteristics of the raw materials in powder are listed in Table 2.

Various sorts of KGL can be manufactured with variable mixing proportions of the raw materials. From the economic point of view four points have been selected in a triangular diagram shown in Fig.2, represented by following three numeral notations, 0.9-30-0.7, 0.7-30-0.7, 0.5-25-0.7 and 0.3-20-0.7. The first numerals represent gypsum/portlandite molar ratio, the second weight percent of gypsum and the last W/S weight ratio.

Thus, specimens having $2 \times 2 \times 8$ cm dimension have been prepared by means of slip casting. Precursors were obtained, demolding after 20 minutes. The precursors were air-dried at room temperature for a few days and then steam-cured at 80°C and 90% R.H. conditions for 24 hours in Tabai steam oven, model LHL-112. Then, XRD and SEM

*According to Bomble⁴⁾, elongation of the heating duration is not so effectable.

Table 1 Chemical composition of Kuroko mining waste and potential minerals calculated.

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	CaO	MgO	Na ₂ O	K ₂ O	BaO	SO ₃	LOS	Total
IA	61.12	0.27	10.01	3.26	0.04	1.30	2.62	0.28	1.82	5.54	8.62	5.43	100.31
Potential minerals; Quartz 59, Chlorite 13, Sericite 19, Barite 9%													

LOS: loss of ignition

Table 2 Physical characteristics of raw materials in powder.

Raw materials	Density, g/cm ³	Fineness, cm ² /g, Blaine
III-anhydrite	—	1,800*
Hemihydrate	2.74**	4,360
Portlandite	2.24**	12,560
Kuroko waste 1A		
R.T.	2.78	3,170
200°C	2.79	3,400
400°C	2.68	1,780
500°C	2.68	1,560
600°C	2.70	1,600
700°C	2.66	1,650
800°C	2.70	1,710
900°C	2.73	3,190
1,000°C	2.69	1,440

*Measured after conversion to hemihydrate. **True density, others, apparent density. R.T., air-dry at room temperature.

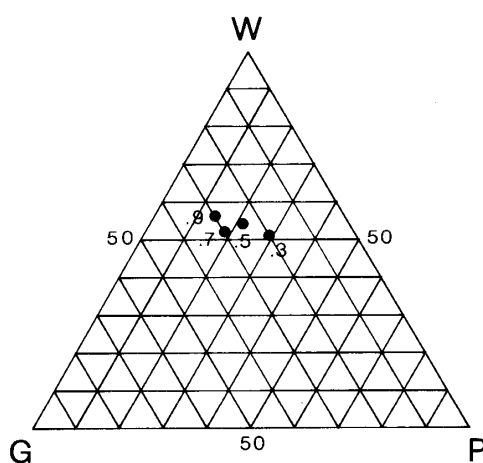


Fig. 2 Triangular diagram showing mixing points, W; waste, G; gypsum, P; portlandite.

investigations were performed, using powdered specimens and brake cut specimens, employing Rigaku X-ray diffractometer, model D-3F and Hitachi scanning electron microscope, model S-510.

3. Results

3.1 Calcined waste in powder

Table 3 lists the results of XRD with special emphasis to the decomposition of the clay minerals by the calcination. According to DTA results, the clay minerals, chlorite and sericite decompose completely above 510°C accompanied by dehydration. However, there still remain those clay minerals intact more or less even after the calcination above this dehydration temperature probably due to nonequilibrium heating conditions, especially the short duration of heating and relatively large amount of charges, generally 90 grams for a crucible.

Fig.3 gives SEM results of the calcined waste in powder, showing relatively coarse grains due to screened through a 100-mesh sieve, opening 149 μ m. The clay minerals take pseudomorphic morphology even after the heat processing. Presence of quartz and barite cannot be so easily distinguished in the photomicrographs.

3.2 Steam cured porous materials

Porous materials having apparent density down to 0.62 have been obtained without blending any bubbling agent, only appropriating mixing water. Strength and thermal conductivity in relevance to apparent density will be published separately.³⁾

XRD investigation showed gypsum and C-S-H as derived hydrates essentially in every specimen irrespective of mixing proportions. Sometimes calcite was identified slightly due to carbonation. No vivid evidence of the reaction of barite has been detected. However, trace presence of Ba(OH)₂.8H₂O and BaCa(CO₃)₂ was encountered in high temperature specimens, i.e., comprising the waste calcined at higher temperatures, but still uncertain.

XRD diagrams are summarized in Fig.4⁵⁾, only for 0.7- and 0.3-series to save space. Other series, 0.9- and 0.5-, also have same trend. No clear presence of the intact clay minerals is detected in high temperature specimens, suggesting that there occur some reactions between the clay minerals and the activators, since some clay minerals remain intact in the waste processed at higher temperatures as mentioned. Sometimes 004 peak of chlorite becomes very much intense, probably due to precalcination and

Table 3 Results of XRD of calcined waste, indicating the intact presence of clay minerals even after high temperature processing.

	R. T.	200	400	500	600	700	800	900	1,000°C
Chlorite	+++	+++	+++	++	++	+	+	+	+
Sericite	+++	+++	++	+++	++	++	+	+	-

Peak of XRD, +++ clearly detectable, ++ detectable, + weakly detectable, - undetectable. R. T., air-dry at room temperature.

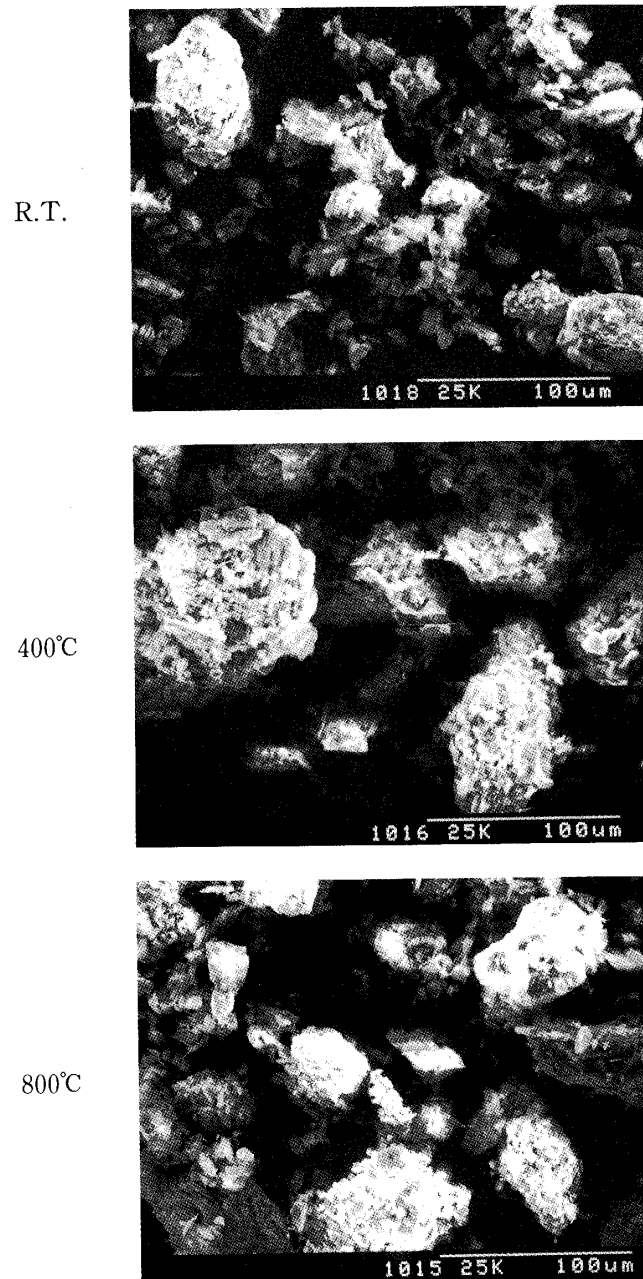


Fig. 3 SEM photomicrographs showing grains of waste calcined.

preferred orientation effects.

Textures of present steam cured porous materials can be classified into two categories in respect to morphology of gypsum. One is low temperature group prepared from the waste calcined at lower temperatures, i.e., room temperature to 400°C. The other is high temperature group prepared from the waste calcined at higher temperatures, i.e., 500°C to 1,000°C.

SEM photomicrographs of the former group are represented in Fig.5 and those of the latter group in Fig.6. At a glance morphological difference of gypsum is remarkable. Gypsum crystals develop generally in irregular platy form in the former group, whereas gypsum crystals develop mainly in acicular to lathlike form in the latter

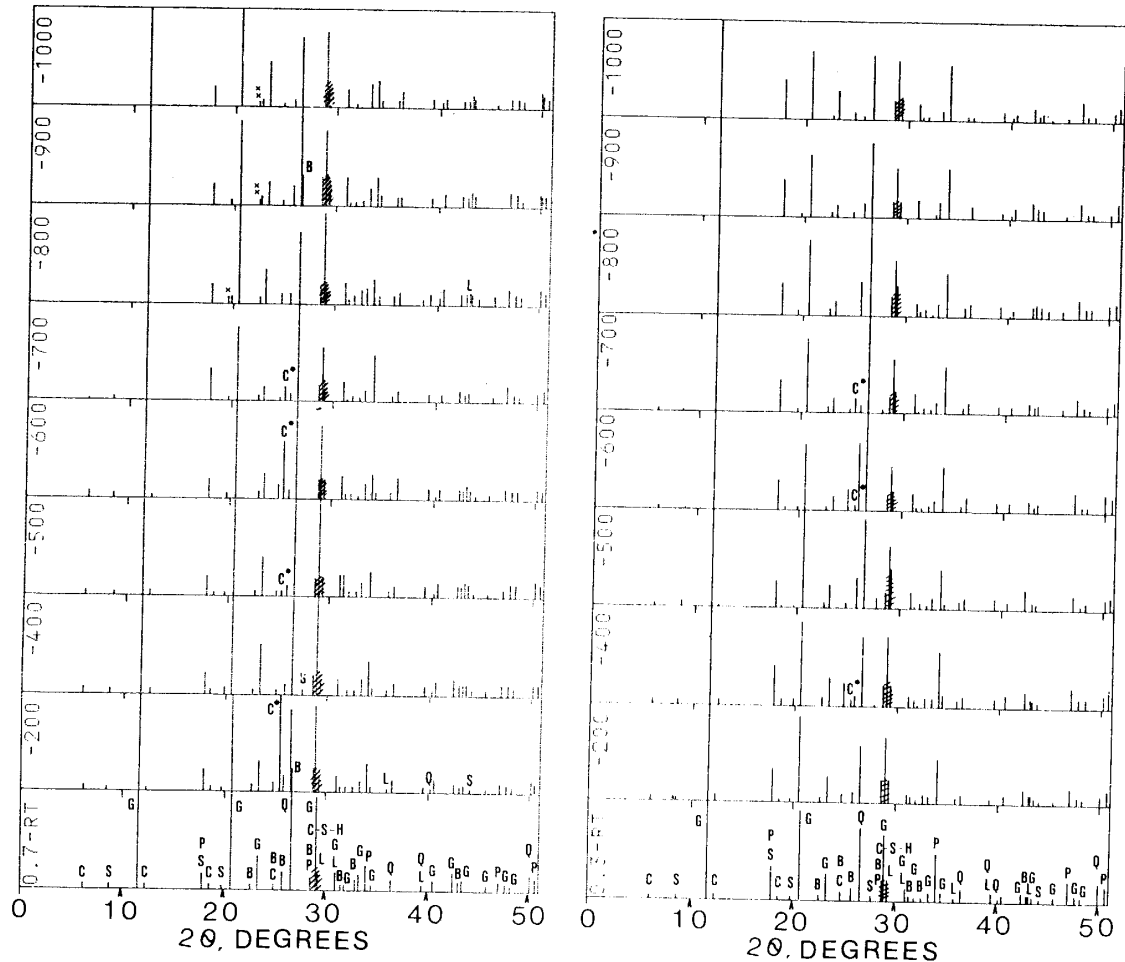


Fig. 4 Summarized XRD diagrams of KGL, only representing 0.7- and 0.3-series due to same trend. Q; quartz, C; chlorite, S; sericite, B; barite, G; gypsum, P; portlandite, L; calcite, C*; 004 reflection of chlorite, x; probable $\text{Ba}(\text{OH})_2$, xx; probable $\text{BaCa}(\text{CO}_3)_2$.

group, which also contributes to the development of strength³). Sometimes the platy gypsum cannot be clearly recognized in the former group. Specimens of 0.3-series have somewhat different trend on the whole probably due to the small amount of III-anhydrite introduced to the initial mixtures. The difference of morphology of derived gypsum may be mainly attributed to ferric ions dissolved in solutions, since high temperature waste may contain much ferric ions, judging from colour change from grey to brown owing to the precalcination in air. Another chemical difference may not exist fundamentally between high temperature group and low temperature group.

Porous textures can clearly be understood from interlocking textures of gypsum in the high temperature group, whereas porous textures cannot clearly be understood in the low temperature group, although the porosity is nearly the same, when the mixing water is constant, irrespective of mixing proportions³).

C-S-H gels are present, adhering on the surface of gypsum crystals point by point. They appear whitish in colour in the photos in aggregates. Presence of remaining portlandite unreacted is not easily distinguished as well as quartz and barite.

3.3 Consideration on the hydration reaction

Gypsum and C-S-H have been found as hydrates after the steam curing.

Under the presence of steam the reaction may be as follows:

- A. III-anhydrite \longrightarrow gypsum
- B. Portlandite + Quartz \longrightarrow C-S-H
- C. Portlandite + Chlorite \longrightarrow C-S-H + X
- D. Portlandite + Sericite \longrightarrow C-S-H + Y
- E. Barite \longrightarrow Barite

Reaction A is quite simple and easy understanding. Barite may not contribute to the hydration as represented in E. Ettringite does not appear in KGL unlike the hydration of fly ash in copresence of gypsum and portlandite⁶⁾.

Reaction B is also very simple and easy understanding, too. Rapid formation of C-S-H is found in steam cured mixture of quartz and portlandite in laboratory tests (unpublished data). Problems are the reactions C and D. C-S-H forms probably through topochemical reactions of clayey pozzolanas. However, the mechanism is quite uncertain at present. X and Y phases should be present as remaining minerals due to leaching of SiO₂ component through topochemical reactions, forming C-S-H around pozzolanas. We encountered C-S-H formation through topochemical reactions as shown in Fig.7. Unfortunately, the core pozzolana is missing, leaving a cocoonlike shell structure. The core mineral is estimated to be quartz from the shape of C-S-H cocoon. However, we have not succeeded yet in detecting the shell structures indicating chlorite and sericite as core minerals.

4. Summary and conclusion

XRD and SEM investigations have been carried out intensively on KGL, novel porous materials prepared from Kuroko mining waste added with gypsum and portlandite. The kuroko waste is better to be processed at moderately high temperatures, 500-1000°C, beforehand. It comprises chlorite, sericite, quartz and barite and the former three minerals act as pozzolana. III-anhydrite was employed instead of gypsum to obtain precursors in a short period of time. The precursors were steam-cured to get water resistant porous materials of light weight. Following results were reached as conclusion:

1) Hydrates are essentially gypsum and C-S-H. No ettringite was found, different from the hydration of fly ash activated with gypsum and portlandite⁶⁾.

2) Textures of present porous materials can be classified into two groups. One is high temperature group and the other is low temperature group. In the former group gypsum develops mainly in acicular to lathlike form, whereas in the latter group that precipitates in irregular platy form.

3) The reason of the morphological difference of gypsum is not clear at present, but ferric ions may act an important role on this phenomenon.

R.T.

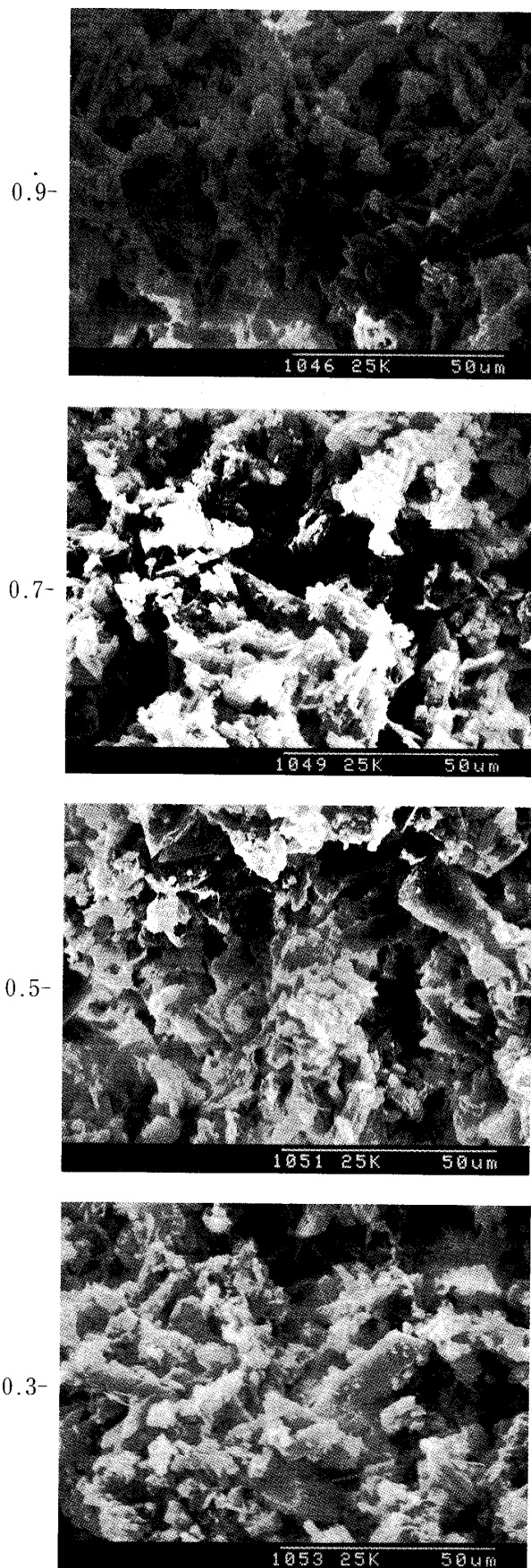
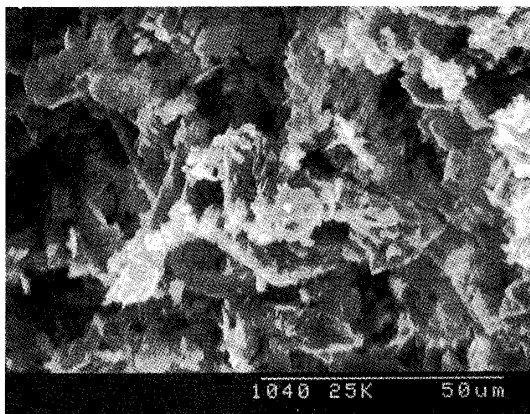
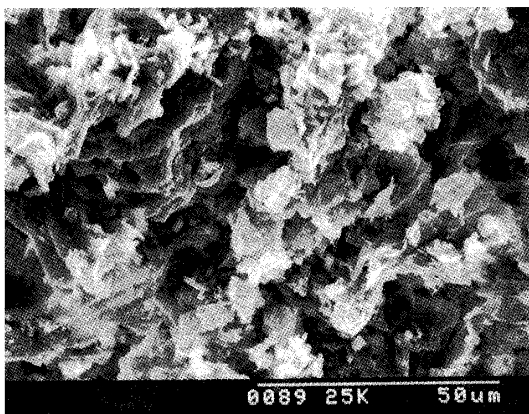


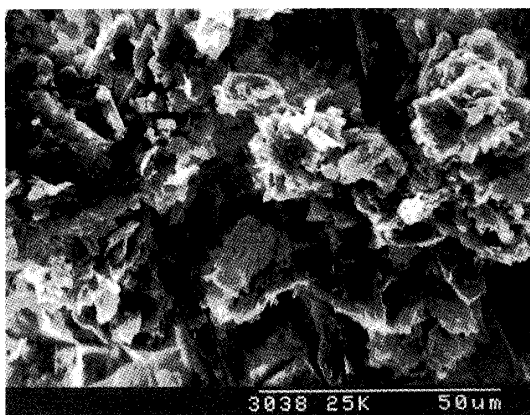
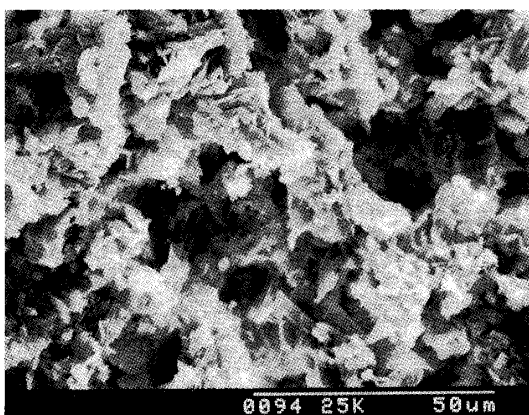
Fig. 5 SEM photomicrographs of low temperature group.

200°C

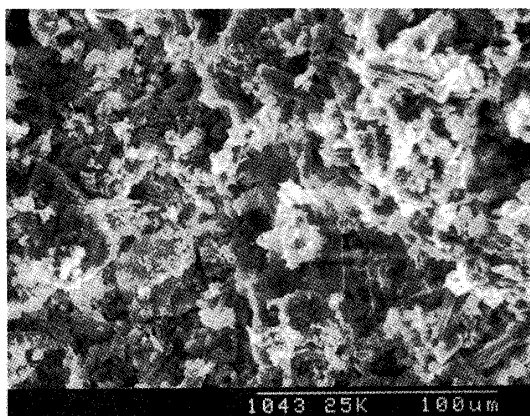
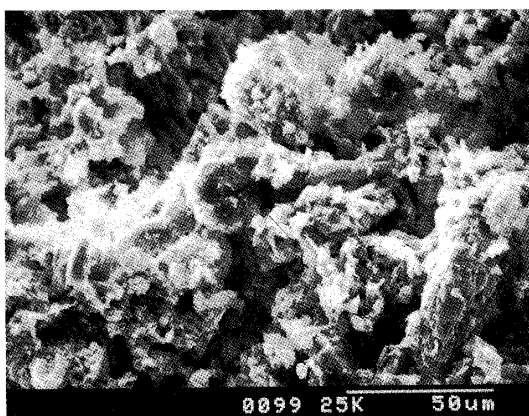
400°C



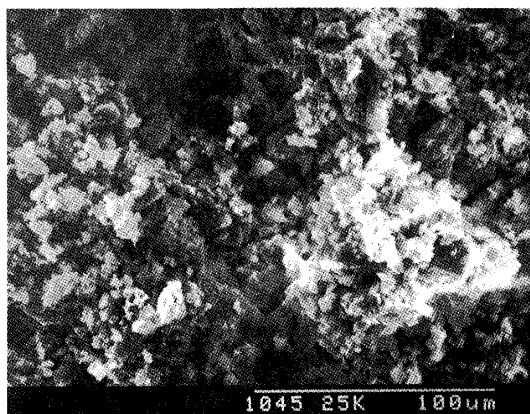
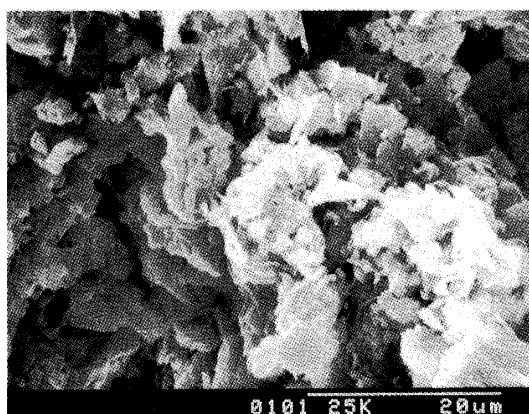
0.9-



0.7-



0.5-



0.3-

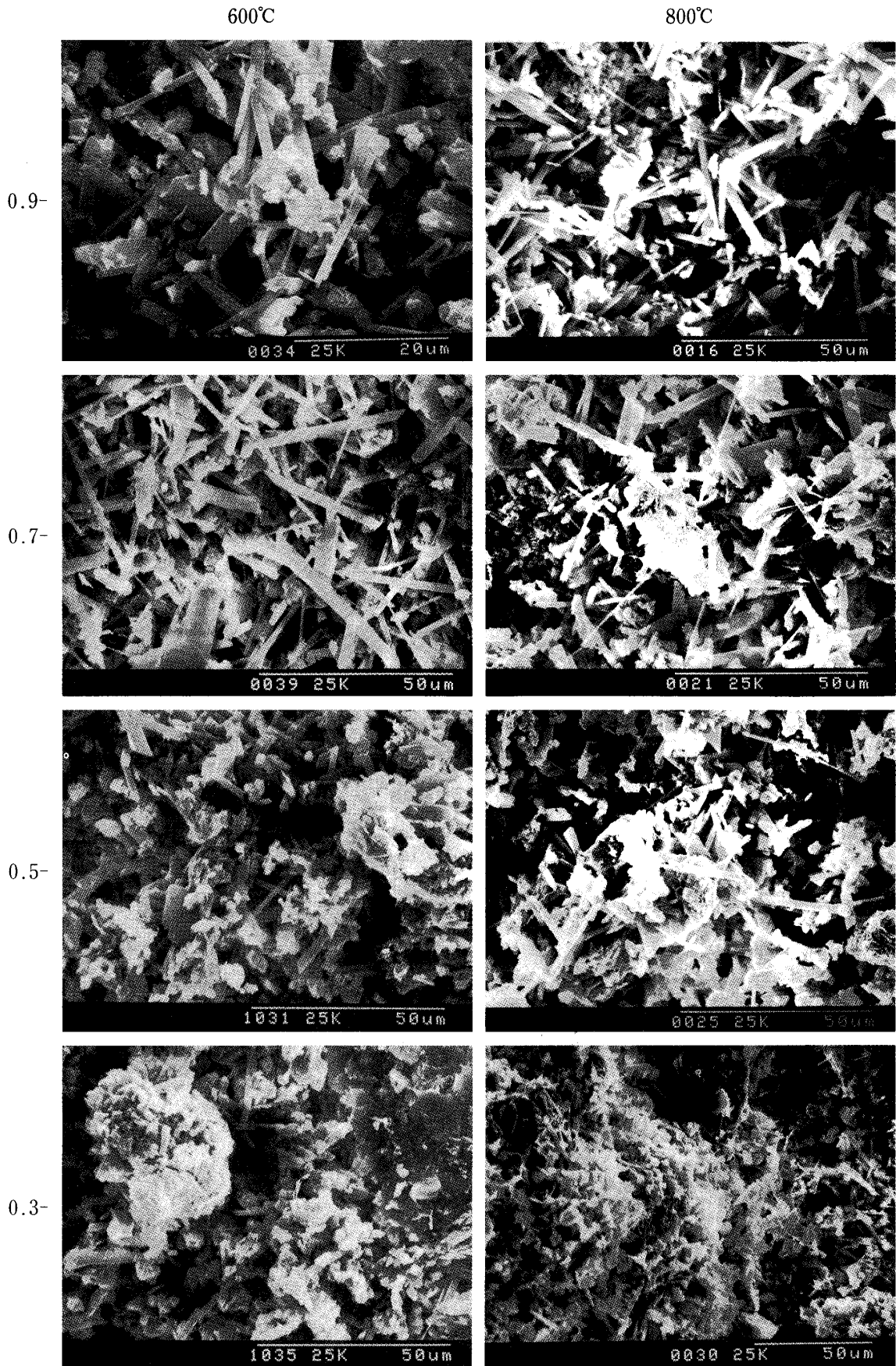


Fig. 6 SEM photomicrographs of high temperature group.

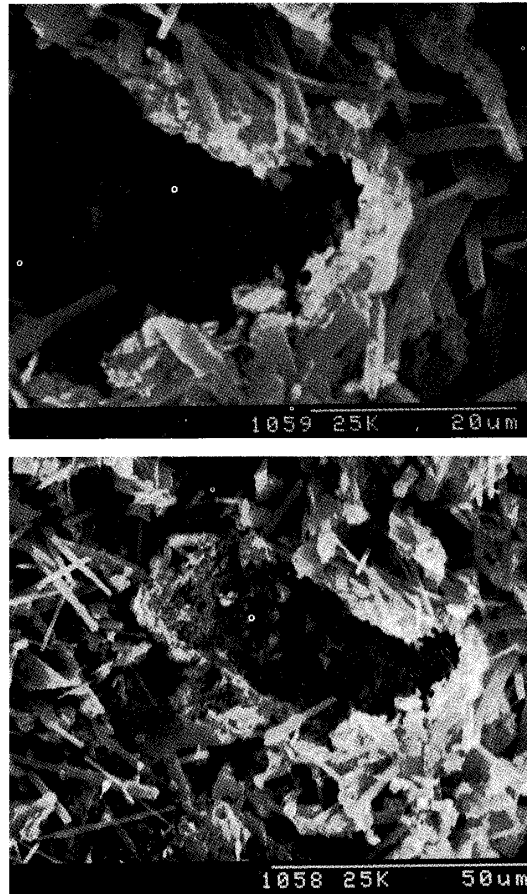


Fig. 7 SEM photomicrographs indicating topochemical reactions of pozzolana, forming cocoonlike shell of C-S-H. Core mineral is missing. Specimen 0.9-30-0.7, 800°C calcination.

4) Hydration mechanism of chlorite and sericite under the presence of gypsum and portlandite is quite uncertain at present.

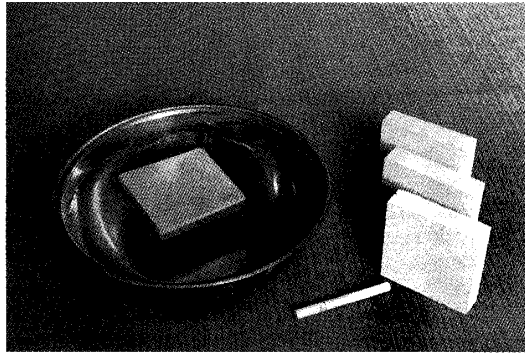
Acknowledgement

The authors express their cordial thanks to Prof. H. Shima for the facilities of SEM. The raw materials of Kuroko mining waste and by-product gypsum were kindly supplied from Hanaoka Mine and Chuden Chemical Engineering Companies, respectively.

References

- 1) Materials of municipal government of Akita Prefecture, "Long distance transportation of Kuroko mining waste (in Japanese)".
- 2) Omori, S., "Artificial light-weight aggregate (in Japanese)", *Ceramics*, 7, 858-864, 1972.
- 3) Ikeda, K., Tashiro, C., Tomisaka, T., "Porous materials prepared from chlorite-sericite-quartz-gypsum-portlandite system by means of steam curing (in Japanese, English version available)", *J.*

- Ceram. Soc. Japan, 98, 216-236, 1990.
- 4) Bomble, J. P., "Différents moyens d'activation des matériaux potentiellement pouzzolaniques. Application aux liants chaux-pouzzolane", Proc. 8th Inter. Cong. Chem. Cement, Rio de Janeiro, 4, 66-73, 1986.
 - 5) Ikeda, K., "An application of a personal computer to the identification and arrangement of powder X-ray diffraction charts in a simplified fashion (in Japanese)", Memorial Papers of Prof. Shibuya on the occasion of his retirement, 1991, (to be published).
 - 6) Ikeda, K., Tomisaka, T., "Fundamental studies on the preparation and strength of steam-cured porous materials made from the mixtures of fly ash, gypsum and lime (in Japanese, English version available)", J.Ceram. Soc. Japan, 97, 478-483, 1989.



Appendix 1. Photo of KGL floating on water.