

Phase Formation from Calcium Aluminosilicate Gels by Soft Hydrothermal Treatment

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Abstract- Several gels in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ were investigated under soft hydrothermal conditions. The gels were synthesized by co-precipitation of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$ and were reacted under the following hydrothermal conditions: sample/solution = 0.03, NaOH concentration = 0 - 4M, temperature = 80 - 150°C and duration = 18 - 192 hours. The phases formed by hydrothermal treatment varied according to the starting compositions, being (1) hydroxysodalite in SiO_2 -rich compositions, (2) hydroxycancrinite in SiO_2 and Al_2O_3 -rich compositions, (3) katoite in CaO and Al_2O_3 -rich compositions and (4) calcium silicate hydrate (C-S-H) in CaO and SiO_2 -rich compositions. The C-S-H phase, which is more amorphous in nature, showed the greatest uptake of Ni^{2+} .

Key words: Calcium aluminosilicate gel, C-S-H phase, hydroxycancrinite, hydroxysodalite, katoite.

1. INTRODUCTION

Because of global environmental issues, the need for a wide variety of adsorbents is increasing. Against this background, interest is growing in adsorbents with multi-functional adsorption properties, e.g. simultaneous acid and base adsorbents, adsorbents for both hydrophilic and hydrophobic molecules, and for both cations and anions.

Zeolites have been successfully utilized in chemical industries and in environmental protection over the last 4 decades, because of their excellent physical and chemical properties, which include molecular sieving, adsorption and cation exchange. Utilization of zeolite in most industrial applications requires certain specifications. In this respect synthetic zeolite can be tailored to meet the strict specifications imposed by adsorption and catalytic processes [1]. Improvement of known applications and the prospect of new applications continue to drive the synthesis of zeolites with new properties and the preparation of composite materials from these [2].

The advantages of sol-gel methods are well known in the preparation of glasses, ceramics, and polycrystalline ceramics. Recent utilization of the principles of colloid, physical and polymer chemistry has contributed a great deal to the understanding of sol-gel technology as a whole. Sol-gel technology offers unlimited potential for the production of high-purity specialized glass films, fibers, and monoliths [3]. Furthermore, the process is useful for preparing powders as the gels can be broken up into granules during the drying step or ground in the dry state to produce granules of high surface area material [4].

The conversion of wastes containing CaO, Al_2O_3 , and SiO_2 to zeolitic compounds such as sodalite, zeolite p, phillipsite, analcime, etc and Al-tobermorite by hydrothermal treatment with NaOH solution has been reported [5]. Further, materials such as Al-tobermorite, sodilite zeolites A and P have useful cation exchange properties.

The objective of this work was to study the products resulting from hydrothermal treatment of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ gels in NaOH solution and to examine their chemical functions such as their cation uptake properties.

2. EXPERIMENTAL

The starting materials were $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$. Gels with different molar ratios of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$ were synthesized by co-precipitation method using NH_4OH as the precipitant. These gels were subjected to hydrothermal treatment under the following conditions: sample/solution = 0.03 g/ml, NaOH concentration = 0 - 4 M, temperature = 80 - 150°C and duration = 18 - 192 h.

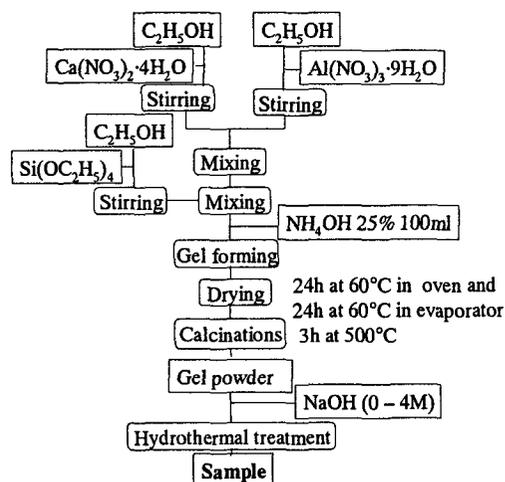


Fig. 1 Schematic diagram of the sample preparation.

The nickel ion uptake properties were investigated by a batch method. 50mL of aqueous $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ solution was mixed with 0.1g of sample and stirred at

room temperature (20°C). The initial Ni^{2+} concentration was varied over the range 10^{-4} to 10^{-2} M. After 24h the sample was washed and separated from the solution by centrifuging. The uptake of Ni^{2+} was calculated from the difference in the Ni concentrations before and after the experiment determined using an ICP-AES plasma spectrometer [SPS-1500VR (Seiko Instruments Inc. Japan)].

XRD measurements were carried out using an XRD-6100 diffractometer (Shimadzu Co. Japan) to examine the crystalline phases formed. The chemical compositions of the samples before and after hydrothermal treatment were analyzed by X-ray fluorescence (RIX2000, Rigaku Co. Japan).

3. RESULTS AND DISCUSSION

3.1 CaO- Al_2O_3 - SiO_2 gels

To obtain various phases from hydrothermal treatment of gels containing the components CaO, Al_2O_3 and SiO_2 , four gels with different molar ratios of CaO, Al_2O_3 and SiO_2 were prepared. The compositions were such as to produce materials that were (1) SiO_2 rich, (2) SiO_2 and Al_2O_3 rich, (3) CaO and Al_2O_3 rich and (4) CaO and SiO_2 rich. The chemical compositions of these gels analyzed by X-ray fluorescence are listed in Table I and their X-ray diffraction (XRD) patterns are shown in Figs. 2(a)-5(a). The presence of a halo in the XRD of the as-prepared samples confirms these to be amorphous.

3.2 Hydrothermal products

The chemical compositions of the as-prepared gels and hydrothermally treated products (sample/solution = 0.03g/ml, NaOH concentration = 4M, temperature = 110°C and duration = 24h for sample No. 1 and 121h for samples 2-4) are listed in Table I. The XRD patterns of these samples are shown in Figs. 2-5.

Table I Chemical composition (mass%) of starting gels and hydrothermal products

Sample No.	Starting gel			Hydrothermal product			
	CaO	Al_2O_3	SiO_2	CaO	Al_2O_3	SiO_2	Na_2O
1	25.7	14.3	60.0	21.8	19.2	45.9	13.1
2	21.1	37.3	41.6	21.2	26.2	40.2	12.4
3	42.2	36.6	21.2	45.3	30.3	20.3	4.1
4	43.2	17.9	39.0	40.5	10.7	41.0	7.8

In sample No. 1, the mass% of CaO and SiO_2 decreased while that of Al_2O_3 increased upon hydrothermal treatment. In addition to these composition changes, a considerable amount of Na_2O is removed from the solution by hydrothermal treatment. The XRD patterns of the hydrothermal products [Fig. 2(b)] show a broad weak peak assigned to calcium silicate hydrate (C-S-H, $\text{CaSiO}_3 \cdot \text{H}_2\text{O}$ JCPDS card No. 34-0002). With increasing NaOH concentration sodium aluminum silicate hydrate [S-A-S-H(I), $\text{Na}_{1.4}\text{Al}_2\text{Si}_{3.9}\text{O}_{11.5} \cdot \text{H}_2\text{O}$, JCPDS card No. 44-0103] was formed. With further increase of the NaOH concentration hydroxysodalite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$, JCPDS card No. 11-401) together with aluminum tobermorite ($\text{Ca}_5\text{Si}_5\text{Al}(\text{OH})\text{O}_{17} \cdot \text{H}_2\text{O}$, JCPDS card No. 19-52) were formed. Increased duration of the hydrothermal treatment favored the formation of aluminum tobermorite.

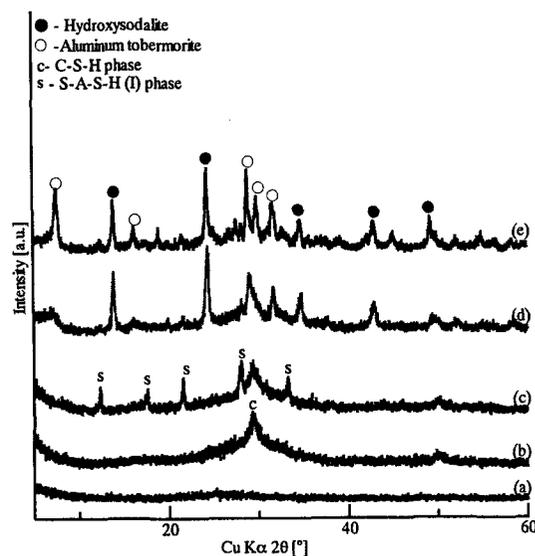


Fig. 2 XRD patterns of sample No. 1 before and after hydrothermal treatment at 110°C (a): as-prepared, (b): 1M NaOH for 24hrs, (c): 2M NaOH for 24hrs, (d): 4M NaOH for 24hrs, and (e): 4M NaOH for 192hrs.

In the case of sample No. 2, the mass% of CaO and SiO_2 remained almost constant while Al_2O_3 decreased after hydrothermal treatment. The XRD patterns of the hydrothermal products are shown in Fig. 3. The product phases are similar irrespective of the hydrothermal conditions. They are sodium aluminum silicate hydrate [S-A-S-H (II), $\text{Na}_{2.12}\text{Al}_2\text{Si}_{1.6}\text{O}_{7.26} \cdot 1.60\text{H}_2\text{O}$, JCPDS card No. 31-1272], hydroxycancrinite [$\text{Na}_9\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ JCPDS card No. 46-1457] and a small amount of C-S-H. Both major products however have the same cancrinite structure. Increasing the NaOH concentration and duration of the hydrothermal treatment increased the amounts of these cancrinite type phases. Hence, more hydroxycancrinite was formed from (b) to (d).

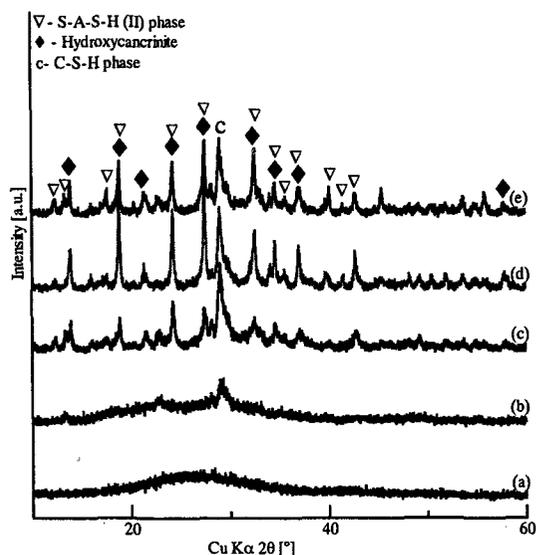


Fig. 3 XRD patterns of sample No. 2 before and after hydrothermal treatment at 110°C (a): as-prepared, (b): 2M NaOH for 24hrs, (c): 4M NaOH for 24hrs, (d): 4M NaOH for 121hrs and (e): 4M NaOH for 192 hrs.

In the case of sample No. 3, only slight changes in the chemical composition resulted from the hydrothermal treatment. The mass% of Al_2O_3 decreased slightly and CaO increased with no change in SiO_2 . The XRD patterns (Fig. 4) show formation of the hydrogarnet group phase katoite [$Ca_3Al_2(SiO_4)(OH)_8$, JCPDS card No. 38-0368] as well as a small amount of S-A-S-H (III) [$Na_{2.16}Al_2Si_{1.68}O_{7.44} \cdot 1.68H_2O$, JCPDS card No. 31-1271]. The product phases were unchanged by varying the NaOH concentration.

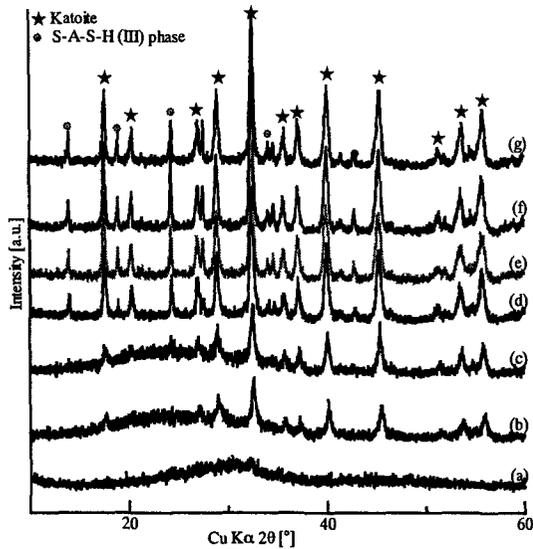


Fig. 4 XRD patterns of sample No. 3 before and after hydrothermal treatment at $110^\circ C$: (a): as-prepared, (b): 1M NaOH for 24hrs, (c): 2M NaOH for 24hrs, (d): 4M NaOH for 24hrs, (e): 4M NaOH 121hrs, (f): 4M NaOH 143hrs and (g): 4M NaOH 192 hrs.

In the case of sample No. 4, the mass% of Al_2O_3 decreased while the concentrations of CaO and SiO_2 were almost unchanged after the hydrothermal treatment. The XRD patterns of the hydrothermal products are shown in Fig. 5. Formation of C-S-H started after treatment with 0.5M NaOH solution and no change was observed in the product with increasing NaOH concentration and duration of the hydrothermal treatment. Although the product contains considerable amounts of Na_2O and Al_2O_3 , it is not certain whether these components are incorporated in the C-S-H phase. It would be necessary to characterize the product using analytical TEM to confirm this.

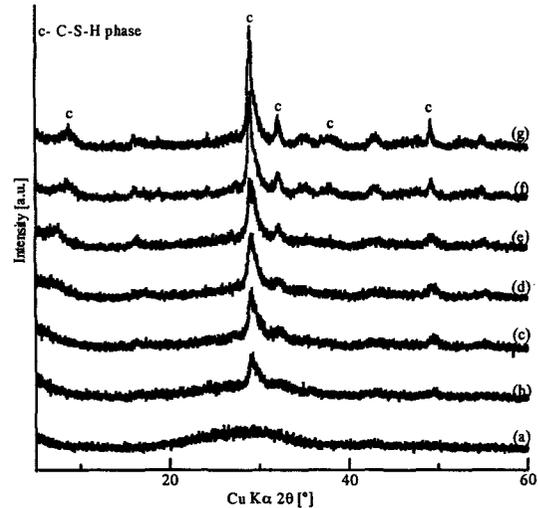


Fig. 5 XRD patterns of sample No. 4 before and after hydrothermal treatment at $110^\circ C$: (a): as-prepared, (b): 0.5M NaOH for 24hrs, (c): 1M NaOH for 24hrs, (d): 2M for 24hrs, (e): 4M NaOH for 24hrs, (f): 4M NaOH for 120hrs and (g): 4M NaOH for 192 hrs.

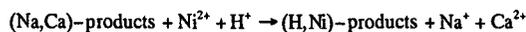
Table II Ni ion uptake by the various samples

Sample No.	Concentration [mM]	pH _i *	pH _f #	Concentration [mM]					Ni ²⁺ uptake		
				Na ⁺	Ca ⁺²	Al ⁺³	Si ⁺⁴	Ni ⁺²	%	[mg/g]	K _d [†]
1-11	23.0	5.27	6.88	5.82	6.78	0.00	0.92	14.6	37	254	288
1-12	17.0	5.46	6.71	5.65	6.44	0.00	0.71	8.9	48	246	455
1-13	12.0	5.40	7.20	3.91	6.18	0.00	1.23	3.68	69	250	1130
1-14	8.7	5.36	7.23	4.26	1.27	0.00	1.02	0.9	90	231	4333
1-15	1.1	5.42	10.51	2.83	0.30	0.00	1.17	00	100	35.8	∞
1-16	0.11	5.48	11.03	2.78	0.12	0.00	1.37	00	100	3.58	∞
2-21	17.0	5.47	6.68	5.74	7.48	0.00	0.28	10.1	41	212	342
2-22	12.0	5.40	6.91	3.70	3.64	0.00	0.48	6.30	48	176	452
2-23	8.7	5.44	7.09	3.61	4.99	0.00	0.32	2.3	73	188	1391
2-24	1.1	5.44	10.34	2.19	0.22	0.05	0.48	00	100	35.8	∞
2-25	0.11	5.36	10.99	2.21	0.20	0.29	0.65	00	100	3.58	∞
3-31	17.0	5.46	7.51	0.26	5.14	0.00	0.00	11.2	35	179	259
3-32	12.0	5.4	7.49	0.26	6.58	0.00	0.00	5.1	57	207	674
3-33	8.7	5.55	7.63	0.27	7.66	0.00	0.00	1.5	83	213	2400
3-34	1.1	5.44	10.92	0.17	1.40	0.03	0.13	00	100	35.8	∞
3-35	0.11	5.36	10.97	0.24	0.37	0.04	0.00	00	100	3.58	∞
4-41	23.0	5.27	6.65	4.87	12.3	0.00	0.71	8.4	63	435	869
4-42	17.0	5.47	7.09	4.79	12.2	0.00	0.64	2.8	84	427	2536
4-43	12.0	5.4	8.81	5.44	2.52	0.00	0.50	00	100	358	∞
4-44	8.7	5.57	9.34	4.91	1.27	0.00	0.35	00	100	257	∞
4-45	1.1	5.46	10.86	1.94	0.47	0.03	0.40	00	100	35.8	∞
4-46	0.11	5.36	11.36	1.67	0.08	0.12	0.37	00	100	3.58	∞

[†]: $K_d = (C_i - C_f) / C_f \times (V/m)$, *: initial pH and #: final pH

3.3 Uptake of Ni ion

The uptake of nickel ion by the four hydrothermal products is listed in Table II. The variation of Ni^{2+} is shown in Fig. 6 as a function of the initial Ni^{2+} concentration. All the products show good uptake ability of Ni^{2+} . Fig. 6 shows that the uptake ability differs in the order: Sample No. 4 > Sample No. 1 > Sample No. 3 > Sample No. 2. The uptake reaction is as follows:



During the uptake reaction, the pH of the solution increases rapidly, and then gradually attains a steady state. This may indicate the formation of a Ni-containing hydroxide-like phase on the surface of the hydrothermal products. This hydroxide-like phase may act as nucleation sites for further uptake of Ni^{2+} .

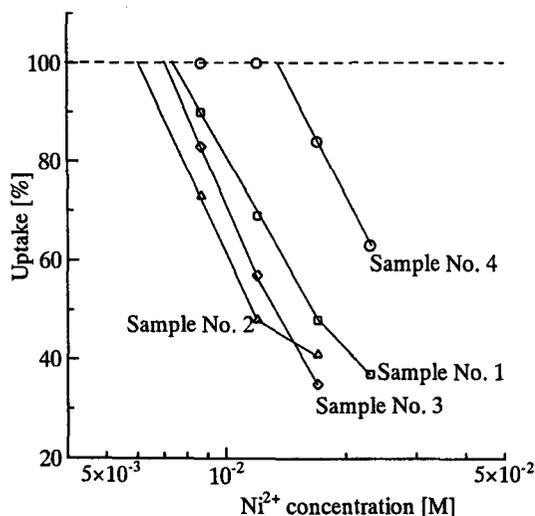


Fig. 6 Change of Ni^{2+} uptake by sample Nos. 1-4 as a function of initial concentration.

4. CONCLUSION

In this study four compositions of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ gels were prepared by a sol-gel method and were hydrothermally treated to form chemically active materials. Various phases such as hydroxysodalite, Altobermorite, hydroxycancrinite, katoite, C-S-H and S-A-S-H phases were obtained by hydrothermal treatment in NaOH solution. The hydrothermal products were found to show good Ni^{2+} uptake behavior. These products are therefore candidates for the removal of heavy metal cations in various solutions.

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