SYNTHESIS OF Na-A ZEOLITE FROM NATURAL ZEOLITES

SARIMAN
R & D Centre for Mineral and Coal Technology
Jalan Jenderal Sudirman No. 623, Bandung 40211
Ph. 022-6030483, fax 022-6003373, e-mail : sariman@tekmira.esdm.go.id

ABSTRACT

Conversion of natural zeolites into Na-A zeolite by the two-step method has been achieved. Synthesis process was conducted at hydrothermal condition 90° and 100° C using alkaline silicates as silica source aluminate as alumina source. The silica was derived from zeolitic tuff and the sodium aluminate was obtained from chemical reagent. Dissolution on zeolitic tuff was made in order to obtain supernatant, $Na_2SiO_3.nH_2O$*. Reaction time for the synthesis ranged from 0.5 – 4 h. It is found that* SiO_2/Al_2O_3 *molar ratio of 1.6,* Na_2O/SiO_2 *molar ratio of 4.41, and* Na_2O/H_2O *molar ratio of 60.70, and crystallization time of 4 h give maximum crystallinity. XRD and SEM showed that Na-A zeolite synthesis begins after 1 h and reaches its crystallization maximum. Then Na-A is substituted by Na-X and hydroxysodalite (HS) zeolite. The XRD pattern and SEM image show that microtextural are comparable to the reputed zeolite commercial.*

1. INTRODUCTION

Research on zeolite synthesis has greatly been developed since zeolite use is extended to several new technological applications. The ion exchange and the selective adsorption properties of zeolites are at the base of several industrial use. Some of them deal with radioactive wastewater treatment, sewage effluent treatment, agricultural-wastewater treatment (Armbruster, 2001; Kang and Egashira 1997; Gobarkar et al.,1999).

The study of Bayah zeolite deposit in the last 30 years shows that the deposit is potential source for mordenite and clinoptilolite have formula of $Na_x(AlO_2)_x(SiO_2)_y.ZH_2O$ and $Na_x(AlO_2)_x(SiO_2)_y.ZH_2O$; the x=5 to 7, y/x=4.5 to 5.5 and Z=1 to 30. However, this natural zeolite is commonly polymineral. Its impurities contain mostly quartz, clay mineral, feldspar and hematite. Such a condition prevents extensive use of this material for industrial process. Therefore, most of these zeolites is useless or at least limited usefulness. Despite this, there is a great economic potential for natural zeolitized rock as substitutes of chemical reagents in zeolite synthesis.

Concerning the synthesis of zeolites using natural raw materials, many natural aluminosilicate minerals such as kaolinite, smectite, halloysite, fly-ash, volcanic glass, natural zeolites have been reported to be the suitable starting materials (Akolekar et al.,1997; Imbert et al., 1994; Fang et at., 1995; Yoshida and Inoueo, 1986). They could readily be synthesized to high-power zeolites such as Na-A zeolite, analcime, zeolite Na-P, faujasite, X, and Y under hydrothermal treatment in a high concentration of NaOH solution. Among those minerals, only the clay kaolinite has been demonstrated to be the most convenient starting materials. It is shown by the number of papers that was reported (de-Lucas et at., 1992; Basaldella et al.,1990; Akolekar et al., 1997). There are three reasons support to this situation namely the easiness in structure transformation from kaolinite to metakaolinite which is known a very reactive mineral structure, no addition of either silica or alumina in the reaction mixture are needed to be used for zeolites synthesis, kaolinite is suitable as starting material for high-grade synthetic zeolites type A (zeolites Na-A) as a cation exchange in a detergent [de-Lucas et al.,1992).

However, until recently, there has been available very little information on the synthesis of zeolite A from natural zeolites. Leonard (1982) tried to synthesise zeolite A from natural zeolite with the addition of sodium aluminate to the reaction mixture. His procedure was improved by Shi (1983) who proposed a two-step method in order to reduce the iron content and undissolved materials. Since this method has the capability of eliminating the impurities in the product, it has been implemented by others for the synthesis of zeolite A from other sources, such as volcanic glasses and pumice (Burriesci et al., 1986; Yoshida and Inoue, 1988).

The two-step method involves dissolution process of aluminosilicate natural raw materials in a sodium hydroxide solution to yield a silica-rich solution. Solution is then mixed with alumina solution to produce aluminosilicate gel. The next step, followed dissolution process is crystallization of the gel under hydrothermal condition to form of synthetic zeolites. The recovery level of this method is dependent on the dissolution rate of the raw materials digested in an alkaline solution.

The work deals with zeolite containing materials to be synthesized using two-step method. Materials used in this work were supplied from Australia and Indonesia. Comparison of both natural zeolites are summarized.

2. MATERIALS AND METHOD

In this study, natural zeolite samples were provided by Zeolite Australia Limited, Level 3 100 Dorcas Street Melbourne VIC 3004 Australia and Research and Development Centre for Mineral and Coal Technology, Bandung Indonesia. The Australian zeolite, a glassy silicate mineral mined at Werris Creek in New South Wales, is a light brown color, while the Indonesian zeolite, mined at Bayah in West Java, is a light green color. Both materials were received in the form of fine particles passing 150 Tyler mesh size.

The used reagent for this study include sodium hydroxide, 99.99 wt% (NaOH) and sodium aluminate ($NaAlO_2$). Both were produced by Ajax Australia 9 Shoat Street Auburn NSW and were used throughout this work. The sodium aluminate contained 36-37 wt % Na_2O and 40-41 wt % Al_2O_3.

Na-A zeolite was used as reference standard. It was obtained from Wako Pure Chemicals Co. 1-2 Doshomachi 3-Chome Chuoku Osaka Japan. Crystallinity of this zeolite was determined based on the high peak XRD intensities. Based on the peaks, no other peaks appear except zeolite A peaks, so its crystallinity is assumed to be 100%.

The synthesis of Na-A zeolite using two-step method was performed according to the method of Shi (1983). This method consists of dissolution of natural zeolite raw materials in sodium hydroxide solution at elevated temperature and after the undissolve solid was separated from the solution, the supernatant was reacted with a certain volume of 15% of sodium aluminate solution at temperature 70°, 90°, and 100°C for various reaction times. The result of synthesis process of the Australian natural zeolite is not presented in this paper.

Dissolution of natural zeolites were carried out at 90° C for various times namely 2, 3, 4, 6, 7 h using 10 wt% sodium hydroxide solution. While for the reaction temperature 100° C, reaction times use was 1, 2, 3, 4, 10, 24, 72, and 120 h using sodium hydroxide solution was 16.6 wt%. The dissolution operation was conducted as follows: 5 g of the natural zeolite was poured in a 200 ml polypropylene bottle containing 100 ml sodium hydroxide solution. The bottle was then sealed and heated in an oven for various times. After this process, filtration of the sample permit to separate a solid, an insoluble fraction and a solution (supernatant as $Na_2SiO_3.nH_2O$). The precipitate was rinsed with distilled water 3 times until pH 10, and dried overnight and weighed. While supernatant was poured into a bottle for use as a starting materials for the synthesis of zeolite.

Synthesizing process was conducted in 50-ml sealed polypropylene bottle by mixing 15 ml sodium aluminate solution 15 wt% to 15 ml supernatant. The mixture was held at 70°, 90°, 100° C for various reaction times that ranged from 0.5 to 4 h. The solid products were then filtered and rinsed using distilled water to remove excess alkali and dried at 105°C for 12 h. Figure 1 illustrates the synthesis procedure .

Chemical composition of the solid raw materials reaction products were determined using Philips X-ray fluorescence unit PW 2400 with Rh Ka radiation and chemical composition of the supernatant from raw materials dissolution was determined using inductively coupled plasma atomic emission (ICP-AES). Mineral species Identification in natural zeolites, Na-A zeolite standard

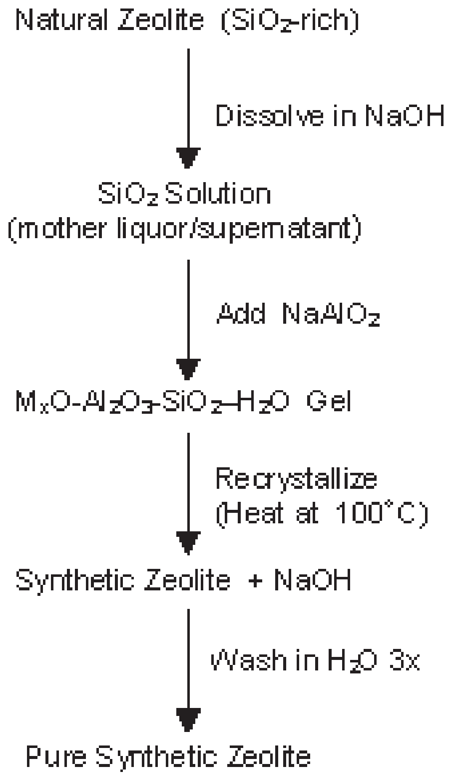

Figure 1. Flow sheet illustrating two-step method for synthesizing zeolite (Shi,1983)

and the product was carried out using Philips X-ray powder diffraction unit PW 1040 with Cu Ka radiation. All samples were finely ground and analyzed whole in a Perspex sample holder. For routine analysis and phases identification, X-ray scans were adjusted in the 5°-50° 2q range at a rate of 1°/min and a step scan of 0.02° 2q. To determine the relative crystallinity, scanning was over the range 11-32° 2q at 1°/min and step scan of 0.02° 2q, as described in ASTM D 5357–98.

Size and morphology analysis of both raw materials and reaction products were performed using Hitachi S-4500, Field Emission Scanning Electron Microscope (FESEM). This unit has an extremely high resolution of down to 1.5 nm, with a tilting stage and a Robson Backscattering Detector. Samples of powder were directly adhered on aluminum stubs using double-sided carbon adhesive tape, followed by gold coating.

The surface areas of the raw materials and reaction products were measured using the single point BET method. Testing was based on the adsorption of nitrogen gas at the boiling point nitrogen. The surface area was calculated from the measurement of the volume, V_m, of the adsorbed nitrogen on a solid surface. By assuming that nitrogen was absorbed in a mono molecular layer, the S_{BET} is determined follows:

$$S_{BET} = \frac{(V_m \times N_o)}{V} \times A \qquad \text{m}^2/\text{g}$$

where:

V = 22,400 mL/mole
N_o = 6.02×10^{23} molecules/mole, The Avogadro Number
A = 15.8 A, the area occupied by a single molecule of nitrogen

3. RESULTS AND DISCUSSION

3.1 Raw materials study

Mineral composition of the two studied zeolites are different (Figure 2). Australian zeolite is clinoptilolite, whereas Indonesian zeolite is mordenite. The ideal chemical formula for those zeolites are [$Na_3K_3(Al_6Si_{30}O_{72}).24H_2O$] and [$Na_8(Al_8Si_{40}O_{96}).24H_2O$] respectively (Breck, 1974:139, 164). Quartz as accessory minerals for both zeolites, was identified in a relatively large quantity. Feldspars presented in a small quantity. Scanning electron micrograph data of both zeolites confirmed the XRD data (Figure 3). In Figure 3 [A] seems that lamellae like structure is clinoptilolite surrounded by feldspars and quartz. Figure 3. [B], showing a small needles like structure, is predicted to mordenite. It is quite hard to identify the existence of clinoptilolite structure. In addition, the presence of amorphous silica (SiO_2) was expected from the broad background pattern at 2q ~ 24-26° .

Chemical compositions of Australian and Indonesian zeolites are listed in Table 1. There are no significant differences between these two zeolites, except for potassium oxide (K_2O). Australian source has more double than that of Indonesian source. The silica contents for both zeolites are really the same (68%), while the silica contents for pure clinoptilolite and mordenite are 30 wt% and 32 wt% respectively. This difference suggests the presence of impurities in the form of silica and feldspar.

The combination of XRD and chemical analysis data, allow the author to use the rational analysis

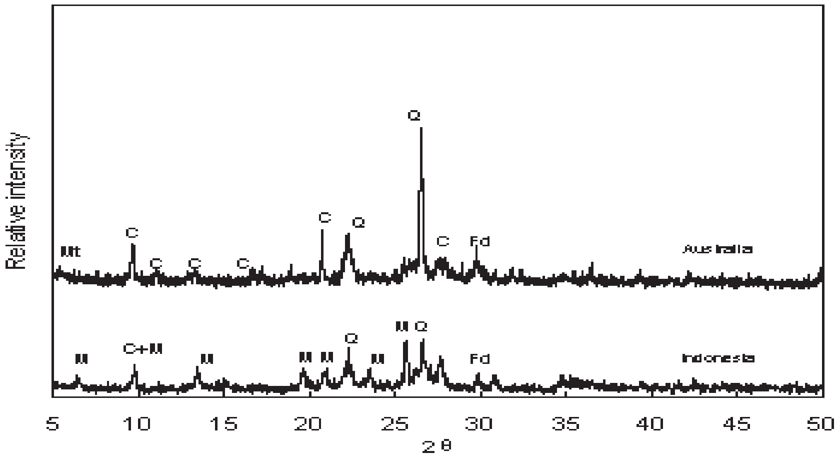

Figure 2. X-ray diffractograms of natural Australian and Indonesian zeolites. M= mordenite, C=clinoptilolite, Q=quartz, and Fd= feldspars, Mt=montmorillonite

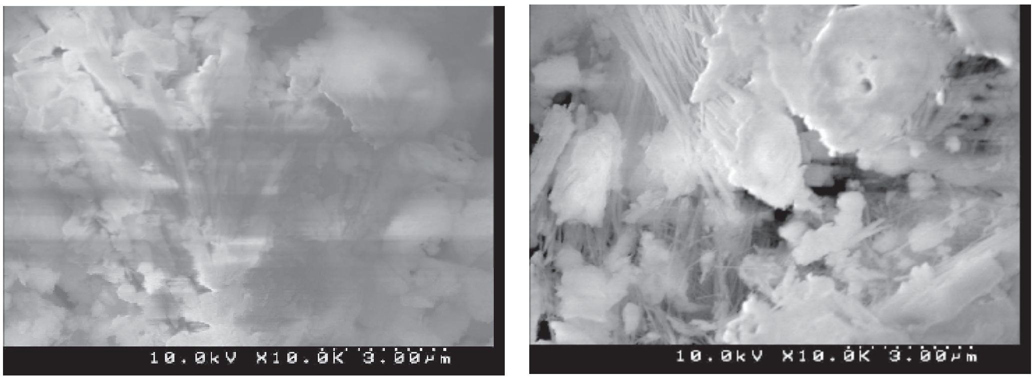

Figure 3. Scanning electron micrograph of Australian [A] and Indonesian [B] natural zeolites, showing lamellae like structure of clinoptilolite and needles like structure of mordenite for zeolite Australia and Indonesia respectively.

Table 1. Major element composition (weight %) of the starting materials used

Zeolite	SiO_2	Al_2O_3	Na_2O	K_2O	MgO	MnO	CaO	TiO_2	Fe_2O_3	LOI
Australia	68.02	11.98	0.29	1.86	1.21	2.8	1.1	0.060.01	1.71	11.04
Indonesia	67.45	12.61	0.19	4.42	0.45	2.15	0.76		1.39	11.2

to determine semi quantitatively. Table 2 shows the minerals amount in the two raw materials. Silica is the highest followed with feldspar and clinoptilolite and mordenite. This result confirm that both zeolites can be categorised as a low-grade.

Table 3 shows the specific surface areas of the raw materials used, demonstrating that the zeolite from Australia has the lower BET surface area. Of the previous SEM micrographs and XRD pattern, it can be seen that many feldspars and quartz present as accessories mineral in those samples. It is known that feldspars and quartz are non-porous materials. As expected, their surface

Table 2. Mineral content in natural zeolites determined using rational analysis

Mineral compositions	Zeolite	
	Indonesia (%)	Australia (%)
Quartz	48.6	58.95
Feldspar	26.14	9.7
Mordenite	2.96	-
Clinoptilolite	-	4.69

Table 3. Specific surface are of zeolites

Sources	BET(m^2/g)
Australia	11.8
Indonesia	36.5

area should be lower.

3.2 Natural Zeolite Dissolution

Dissolution experimental conditions and chemical analysis of mother liquor is listed in Table 4.

3.2.1 Effect of Alkaline Concentration

Results of dissolution studies on natural zeolites are given in Figures 4 and 5. These show the change in molar concentration of SiO_2 (C_{SiO2}) and Al_2O_3 (C_{Al2O3}),in the liquid phase during the dissolution of the natural zeolite in 10% and 16.6% of NaOH solution at 100°C. General observation can be made:

1) the model of dissolution process on this particular zeolite (clinoptilolite and mordenite) is more likely one stage model, meaning no induction time required. This model, regardless the time needed to get an equilibrium stage, indicates this natural zeolite dissolution is similar with that obtained from amorphous aluminosilicate precursor when that is dissolved in alkaline solution (Antonic et al.,1993, 1994).
2) Dissolution rate increases dramatically with increasing concentration of sodium hydroxide solution.

3) The maximum silica concentration is almost four times with increasing concentration of sodium hydroxide from 10% to 16.6% for digestion temperature 100°C

Table 4 Dissolution experimental conditions and chemical analysis of mother liquor (supernatant)

Mother liquor	Experimental conditions for the dissolution process of natural zeolite			Chemical analysis (ppm)			
	NaOH %	t (h)	T (°C)	SiO_2	Al_2O_3	Na_2O	Fe_2O_3
1	10	2	90	3468	57.34	2934	1.44
2	10	4	90	3455	45.05	2923	2.59
3	10	5	90	3520	57	2587	4.48
4	10	6	90	3940	53.69	22576	0.68
5	10	7	90	3966	41.9	2742	2.45
6	16.6	2	70	8828	962.9	23460	9.38
7	16.6	4	70	11350	1005	24090	12.55
8	16.6	2	90	7649	176.9	43996	7.25
9	16.6	4	90	9762	170	43647	11.75
10	16.6	6	90	9853	159.2	42912	7.94
11	16.6	1	100	8773	1076	33120	7.57
12	16.6	2	100	9563	624.4	32880	9.54
13	16.6	3	100	10170	324.2	32490	18
14	16.6	4	100	10320	26.99	32070	15.7
15	16.6	10	100	11380	17.24	31810	22.25
16	16.6	24	100	11640	192.4	31270	16.51
17	16.6	72	100	10920	173.3	31750	18.12
18	16.6	120	100	13710	156.5	25740	16.79
19	16.6	6	90	8964	171.7	40813	14.58

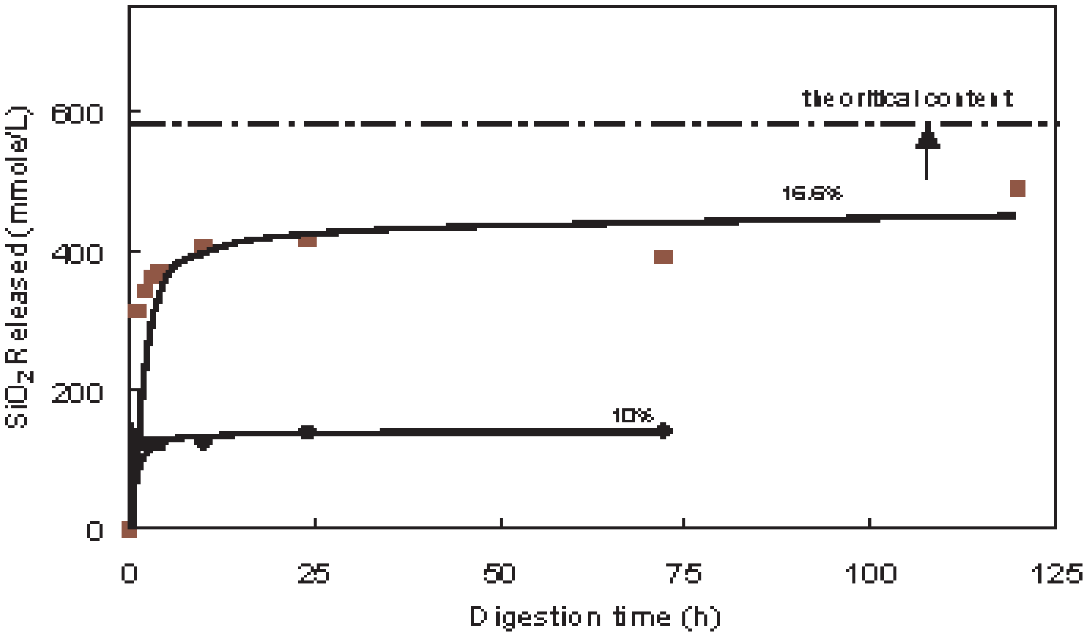

Figure 4. Plot of silica concentration released into the solution from dissolution of natural zeolite in 10% and 16.6% NaOH solution at 100°C. ¡%=16.6%, Ê%=10%

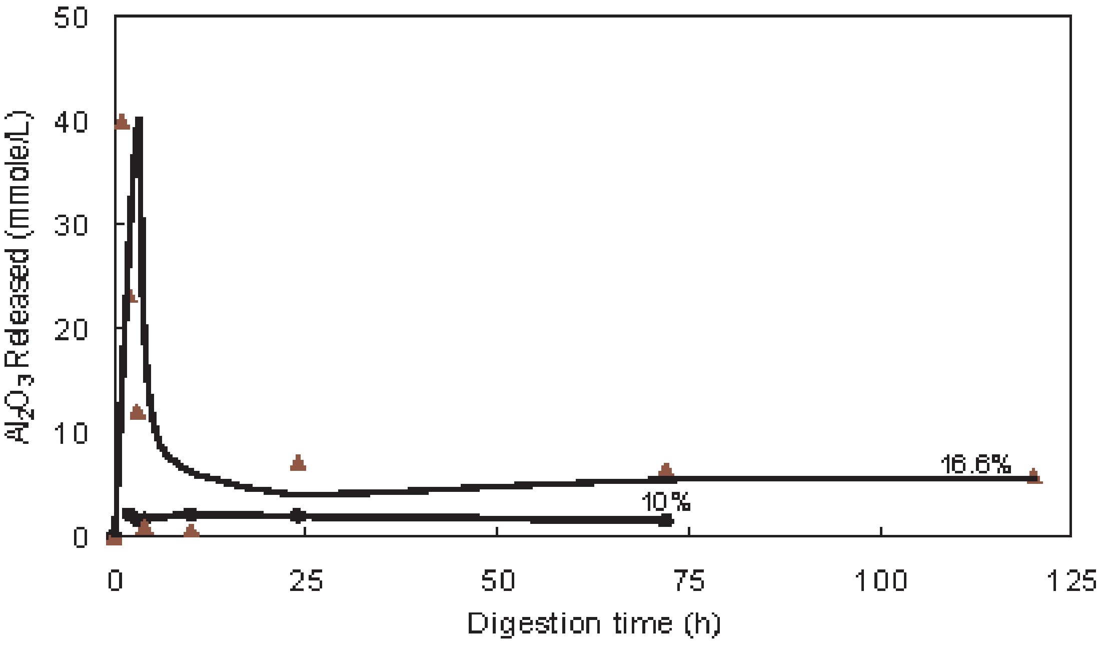

Figure 5. Plot of alumina concentration released into the solution from dissolution of natural zeolite in 10% and 16.6% NaOH solution at 100°C, “=16.6%, ª%=10%

As expected, the dissolved concentration of natural zeolite in solution increases by increasing the alkaline concentration and it is clearly indicated by the shifting the equilibrium concentration position into a higher value of that zeolite, as demonstrated in Table 5. For example the equilibrium concentration of silica was 140 milimol/liter for dissolution time 20 h under 10% concentration of NaOH solution, on the other by using 16.6% of that solution, the equilibrium concentration of silica become 415mmol/Liter for the same time of dissolution. Similar effect also took place for alumina. Since the sample used in this experiment was 5 g in 100 g of solution, note 100 g of solution = 96 ml. The theoretical concentration of silica in that solution was 591.6 milimol/liter. Thus the amount of the dissolved silica in solution was 67% and 20% for the concentration of NaOH solution used 16.6% and 10% respectively. The molar ratio of silica to alumina, SiO_2 /Al_2O_3 at the equilibrium state in the liquid phase is >> 1. In this case, it suggests that silica dissolution was in favour at high alkaline solution.

Table 5. Equilibrium concentrations of silica C^*_{SiO2}, and alumina C^*_{Al2O3}, determined in the liquid phase during the dissolution of natural zeolite in 10% and16.6% NaOH solution at 100°C

Concentrations (%)	C^*_{SiO2} (milimol/l)	C^*_{Al2O3} (milimol/l)	$\frac{SiO_2}{Al_2O_3}$
10	140	1.5	93.33
16.6	415	6.4	64.84

The dissolution of X, synthetic mordenite and aluminosilicate precursor under hot NaOH solution showed relatively incongruent of the amount of both silica and alumina dissolved in the liquid phase (Czismek et al.,1996). The similar situation for the dissolution rate of silica and alumina in natural zeolite occured, indicated by the maximum silica concentration achieved about 490 milimol/liter. Meanwhile the amount of alumina dissolved at equilibrium phase was only 5.79 milimol/liter at the use of sodium hydroxide concentration 16.6%. Similar pattern also happened for lower concentration (10%). Concentrations of silica and alumina dissolved were 140 milimol/liter and 1.55 milimol/liter respectively. According to Dmitrevskii et al. (1971) the solubility of silica in alkaline is inversely proportional with the presence of aluminate ion. Further possibility explanation offered by Alexander et al. (1954), Lechert et al. (1993) postulated that because of negatively in charged tetrahedra alumina centre, It caused relatively inert to hydroxide attack. It promoted that the stability of Si-O-Si bond was lower than that of Si-O-Al bond. As a result, a broken original structure would occur. Rearrangement of that bonds facilitated a formation of new phase during the dissolution process.

3.2.2 Effect of Temperature

Figure 6 and 7 demonstrates the change in molar concentration of SiO_2 (C_{Si}) and Al_2O_3 ($C_{Al,}$), in the liquid phase during the dissolution of natural zeolite in 16.6% NaOH for two different temperatures 90° and 100°C. Broadly, there is a less pronounce on the releasing of alumina, but a little bit significance for silica from natural zeolite in respect to the temperature of dissolution. Table 6 shows that the equilibrium concentration of silica $C^*_{SiO2,}$ and of alumina $C^*_{Al2O3,}$ in the liquid phase markedly depend on the dissolution temperature. As expected from the change of SiO_2.

Figure 7 shows, a very fast dissolution occurs for dissolution time below 5 h and after that for the following dissolution time, it declines dramatically and remains constant to the concentration of Al_2O_3 of 6.4 mmol/l. This phenomenon can be explained as follows; when the silicon and aluminium from dissolution process realising to the solution, a re-arrangement of silicon and aluminium in the solution occur and at a saturation condition a new phase forms. As a result, most of aluminium is consumed leaving of aluminum in the solution in a small amount. The new phase was identified as hydroxysodalite (result is not shown here).

Table 6. Equilibrium concentrations of silica C^*_{SiO2}, and alumina C^*_{Al2O3}, determined for the liquid phase during the dissolution of natural zeolite in 16.6% NaOH solution at two different temperatures

Concentrations (%)	C^*_{SiO2} (milimol/l)	C^*_{Al2O3} (milimol/l)	$\frac{SiO_2}{Al_2O_3}$
10	352	5.9	5.9
100	415	6.4	6.4

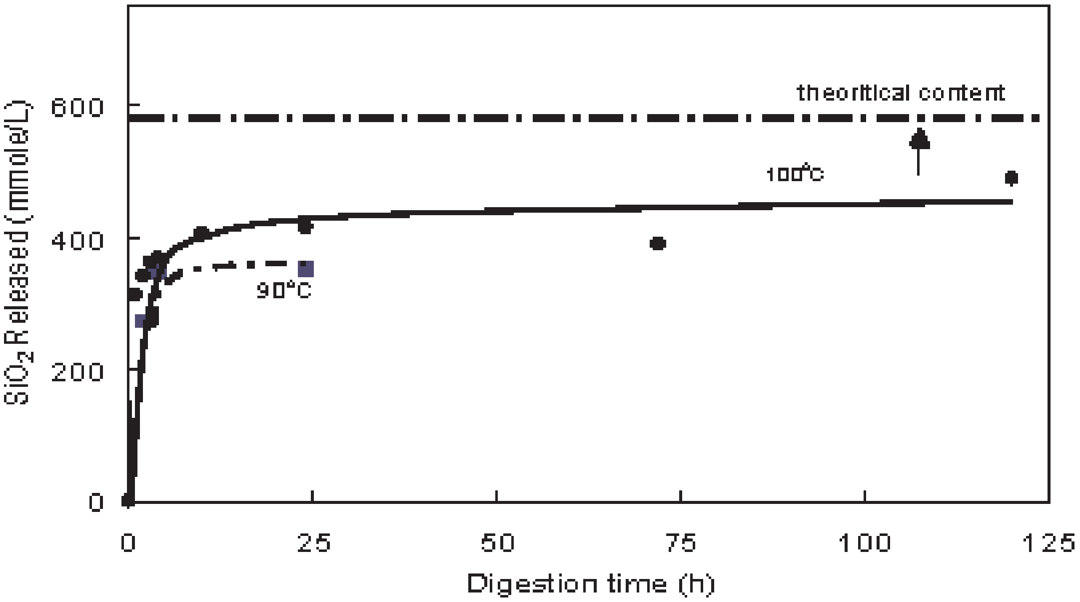

Figure 6. Plot of silica concentration for the dissolution of natural zeolite as a function of temperature in 16.6% NaOH solution. “=90°C, Ê%=100°C

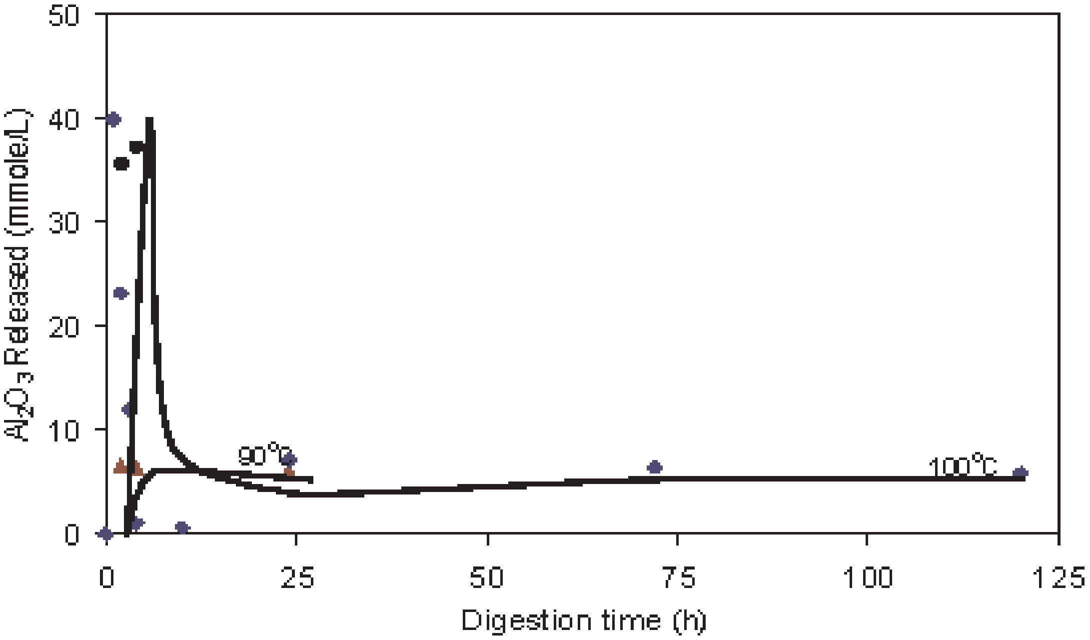

Figure 7. Plot of Alumina concentration for the dissolution of natural zeolite as a function of temperature in 16.6% NaOH solution: “=90°C, Ê%=100°C

3.3 Synthesis of zeolite

3.3.1 Effect of SiO_2/Al_2O_3

Crystallization of zeolite using Shi two-step method was carried out initially by means of direct digestion of the raw materials in alkaline solutions and the supernatant obtained was then subjected to hydrothermal reaction. Table 4 shows the details of the digestion process and the chemical composition of the resultant supernatant. It can be seen that there is an extremely low Fe content in the supernatant (<25 ppm). It suggests that the zeolite formed is high purity. In addition, the SiO_2/Al_2O_3 ratio of the liquid is much higher (~ 100) than in the starting materials (~ 5) due to the higher solubility of SiO_2 in comparison to Al_2O_3, as discussed previously. It means that in order to crystallize Na-A zeolite from this supernatant, a high amount of Al_2O_3 in the form of sodium aluminate is needed.

After modification of the Al content in the supernatant, the molar ratio of SiO_2/Al_2O_3, Na_2O/SiO_2, and H_2O/Na_2O in the solutions varies between: 0.6-3.7; 3.1-8.7; and 60.7-67.8 respectively. Details of the molar ratio composition and resulted zeolite species are listed in Table 7. Figure 8 shows the formation of hydroxysodalite, zeolite X, and zeolite as a function of the composition of the reactant solution. The mother liquor used in the formation of these zeolites was no. 8, 11, and 19 (Table 7).

The data show that the final molar ratio composition of the solution required for formation of zeolite A, varied in the range: SiO_2/Al_2O_3= 0.6-2.0; Na_2O/SiO_2= 3.7-6.0; and H_2O/Na_2O = 60-68.5. The ranges of molar ratios obtained were somewhat different from those of other authors (Imbert et al.,1994) since they used pumice as starting material. Their molar composition range were SiO_2/Al_2O_3 = 0.9-1.8; Na_2O/SiO_2= 2.2-4.2; and H_2O/Na_2O = 60-90. Compared to the SiO_2/Al_2O_3 ratio for sample prepared by fusion (0.2-0.8), the range for the ratio obtained using the two-step method is wider than that from fusion. It would be said that gel obtained using two step method much reactive than that produced from fusion method. Or in other word, most of silicon and aluminium ion in the solution is readily in formation of aluminosilicate compound. It is also supported from visual observation, in which the formation of creamy aluminosilicate gel was immediately occurred after mixing of silica and aluminate sources.

Table 7. Calculated molar ratio compositions of final mother liquor used and the zeolites species obtained

Mother liquor	Final molar ratio			zeolites species formed
	SiO_2/Al_2O_3	Na_2O/SiO_2	Na_2O/H_2O	
2	1.4381	8.7462	59.9594	X, A
3	1.4651	8.5847	59.9523	X, A
4	1.6399	7.6696	59.9059	X, A
5	1.6507	7.6193	59.9031	X, A
8	1.1939	5.0116	62.4647	A
8	1.8572	4.4192	60.7409	A
11	0.6087	6.0273	67.8749	A
11	0.9131	4.943	66.2406	A
11	1.3696	4.2201	64.6846	A, HS
11	2.1305	3.7038	63.2012	A, HS
11	3.6524	3.3165	61.7855	HS
19	0.6218	5.8403	68.5959	A
19	0.9328	4.7789	67.1013	A
19	1.3991	4.0712	65.6719	A
19	2.1764	3.5657	64.3035	HS
19	3.731	3.1866	62.9924	HS

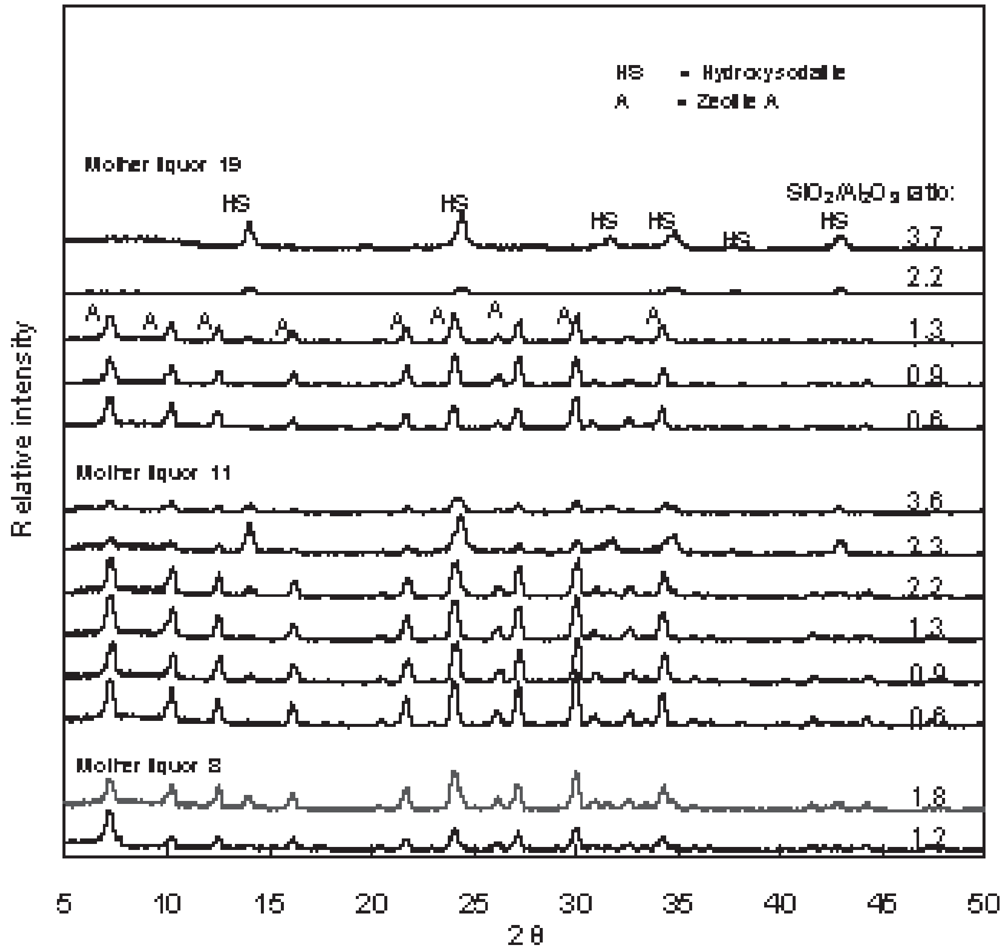

Figure 8. X-ray diffractograms of various zeolites resulting after the supernatant were reacted with 15% aluminate solution

At SiO_2/Al_2O_3 ratio > 2.0 (mother liquor 11 and 19), the XRD patterns obtained (Figure 8) demonstrate the transformation of zeolite A into hydroxysodalite. This is due to the increase in the SiO_2/Al_2O_3 ratio and, when that ratio is further increased, single phase of hydroxysodalite replaces zeolite A. This is expected since the SiO_2/Al_2O_3 ratio of hydroxysodalite is higher than that of zeolite A (Breck, 1974:305). Figure 9 shows micrographs of hydroxysodalite zeolite resulted in "*cotton ball*" type of morphology (Benning et al.,2000). The sample in Figure 9 [A] was obtained from the transformation process of zeolite A due to the change in the SiO_2/Al_2O_3 ratio, while Figure 9 [B] shows the product of the transformation from natural zeolite due to the dissolution process. The latter product indicates that the transformation has just started to occur, as can be seen by the presence of amorphous materials around those particles.

Sobotic et al. (1980) states that the transformation of zeolite A into hydroxysodalite depends, mainly on the concentration of alkali, temperature and time of reaction. But the SiO_2/Al_2O_3 ratio also another factor that should be considered as found in this work.

Figure 10 shows the reaction product as a combination of zeolite X and A. The product resulted from the natural zeolite after digestion process in 10% NaOH solution at 90 °C for 4 h (mother liquor 2). SEM observation as shown in Figure 11 reveals the predominant of zeolite X. There is also some zeolite A and amorphous phases. At longer crystallization time, the zeolite A disappears but the amorphous phase is retained as shown in Figure 11 [C].

According to the range of the SiO_2/Al_2O_3 ratio used, the zeolite that should have formed was

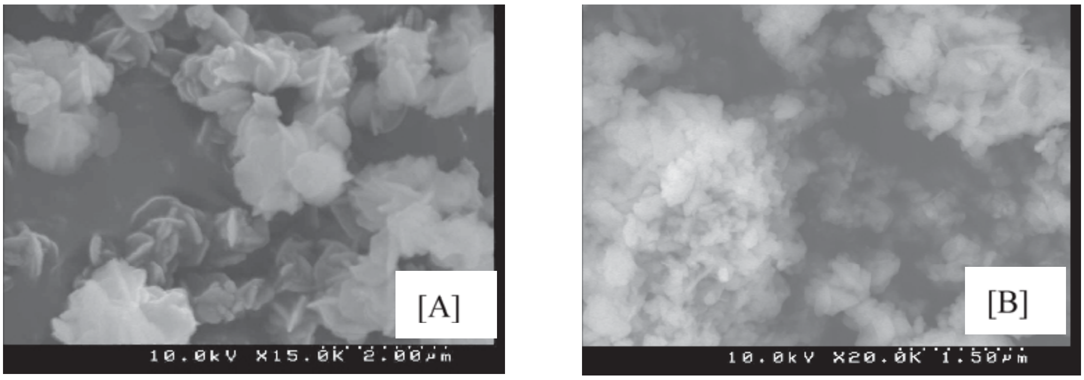

Figure 9. **SEM micrographs of hydroxysodalite obtained from transformation of zeolite A [A] and transformation of natural zeolite [B].**

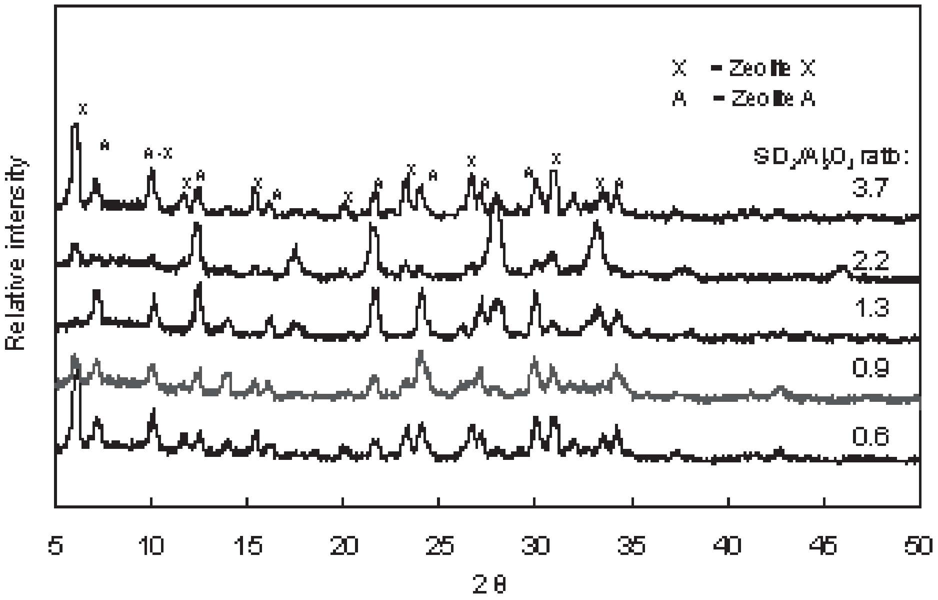

Figure 10. X-ray diffractograms of various zeolites resulting after the supernatant was reacted with aluminate. Reaction condition was 10% NaOH, 90 °C for 4 h

zeolite A. There are two reasons for this anomaly; the Na_2O/SiO_2 molar ratio and the potassium content (K_2O). It has been reported that the combination of higher Na^+ and lower K^+ content encourages crystallization of zeolite X (Roozeboom et al.,1987).

3.3.2 Time of Reaction

The crystallization rate for zeolite obtained from the two-step method using mother liquor 11, is illustrated in Figure 12. It shows that zeolite particles appear after 0.5 h of reaction and this crystalline solid still is retained until 3.5 h, having size in varying from 1–1.5 mm, and agglomerate to each other. However, up to 3 h, unreacted amorphous solid is retained as seen in Figure 13. This means that the conversion of the amorphous to the crystalline phase was not completed. Compared to the fusion method, the growth of the crystalline phase using this two-step method is faster than that of the fusion method. The rate of crystal growth by fusion method needed at least 5 h of crystallization time in order to get a certain in size of crystalline to be analyzed by XRD method.

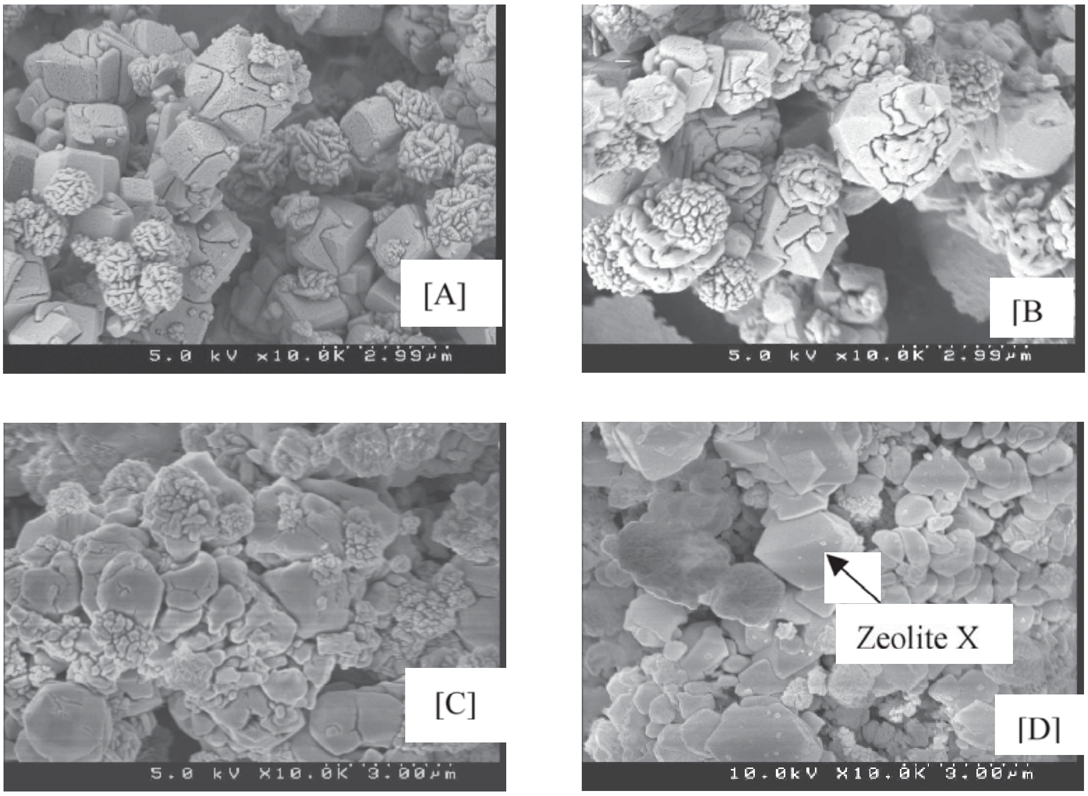

Figure 11. **SEM micrographs of zeolite X+A resulting from the two-step method with molar SiO_2/Al_2O_3 = 1.65, Na_2O/SiO_2 = 7.61, H_2O/Na_2O = 59.9 [A]; and SiO_2/Al_2O_3 = 1.43, Na_2O/SiO_2 = 8.7, H_2O/Na_2O = 59.9 [B]. Crystallization condition 4 h and 90°C. [C] and [D] similar in composition to [B] but crystallization time was extended to 6 and 8 h, respectively**

3.3.3 Morphology of Zeolite Obtained

Figure 14 shows the crystal morphology of the products obtained from two-step system. [A], The regular cubes (~ 2.6 mm), shows sharp edges. No indication the existence of amorphous phase. [B], the commercial crystalline of zeolite A was used as a standard in this experiment. The crystalline from the two step method product showed almost as the same as crystalline of zeolite commercial. This result confirms with XRD pattern as shown in Figure 15.

Referring to the color of the obtained zeolites, the commercial zeolite is as white as that from the two-step method. It is well known that to some extent the iron content present in the starting materials of synthesis zeolite, affects the whiteness of the zeolite formed. As listed in Table 1, iron content in the reaction mixture is very low. Furthermore, the produced zeolite using this starting materials is suitable in the formation of zeolite.

4. CONCLUSIONS

Conclusions regarding this work are as follows:

- Starting dissolution rate increases with dissolution concentration and temperature, but in the equilibrium stage the rate of dissolution is dependent on the dissolution temperature.
- Choice of reaction condition is of special importance for the investigation of the zeolites formation.
- Suitable condition in the formation of high purity of Na-A zeolite was the SiO_2/Al_2O_3 molar ratio of 1.6, Na_2O/SiO_2 molar ratio of 4.41, and Na_2O/H_2O molar ratio of 60.70.
- The Na-A zeolite obtained are comparable with the commercial zeolite.

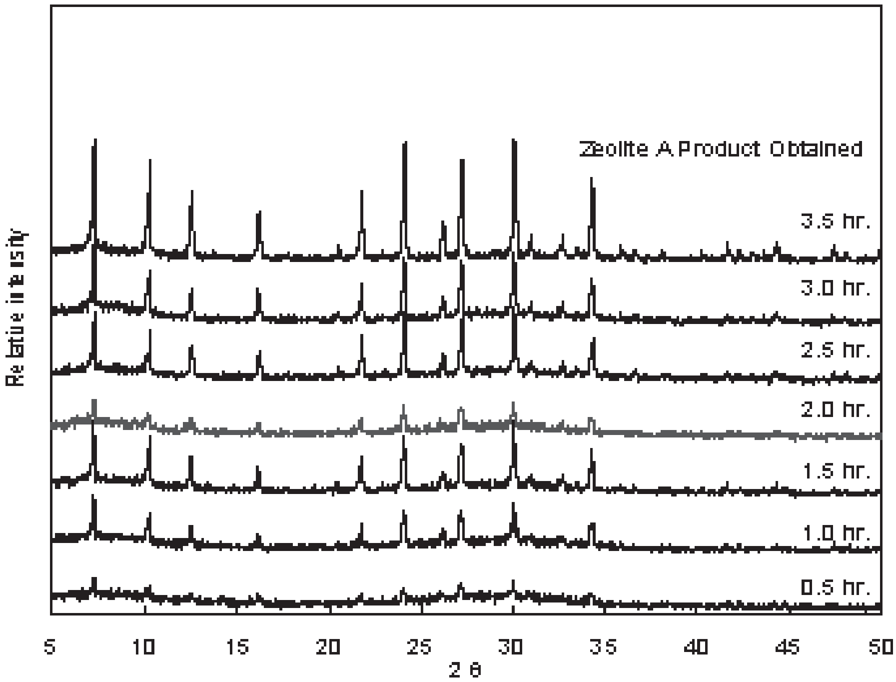

Figure 12. X-ray diffractograms of zeolite A using the two-step method as a function of times

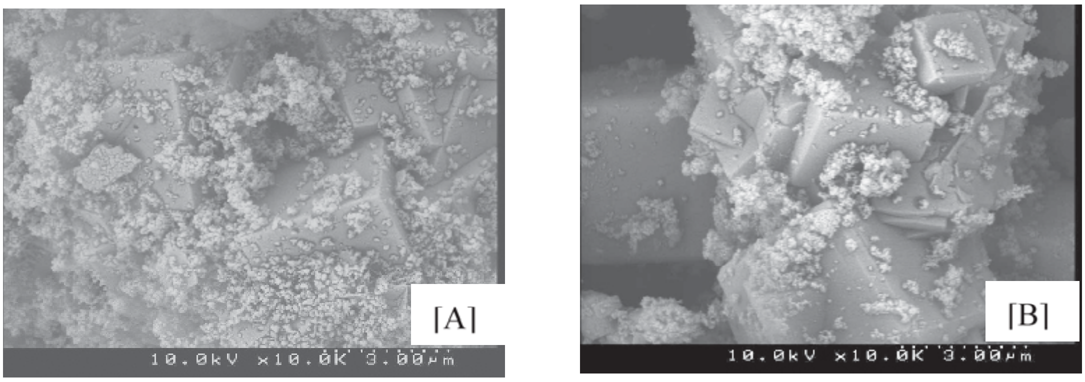

Figure 13. SEM micrographs showing the growth of zeolite A after 0.5 h [A] and after 3 h [B]

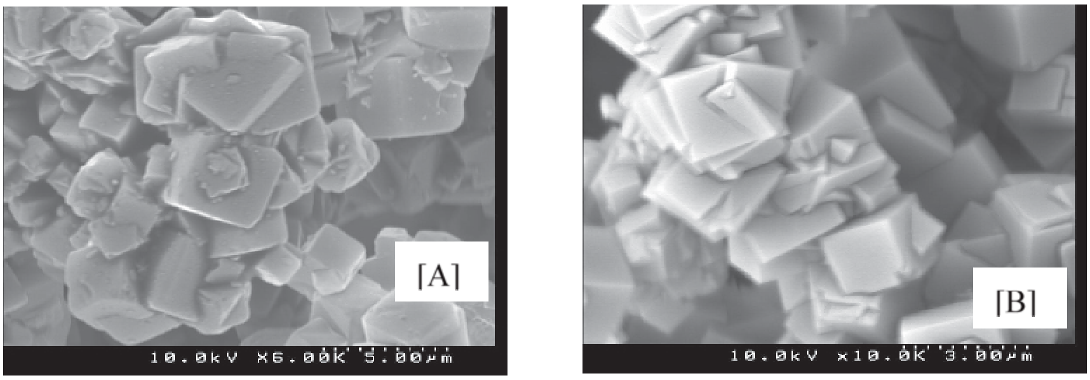

Figure 14. SEM micrographs showing zeolite A obtained [A], by two-step method and [B], commercial zeolite A. Reaction condition: 100°C and 5 h

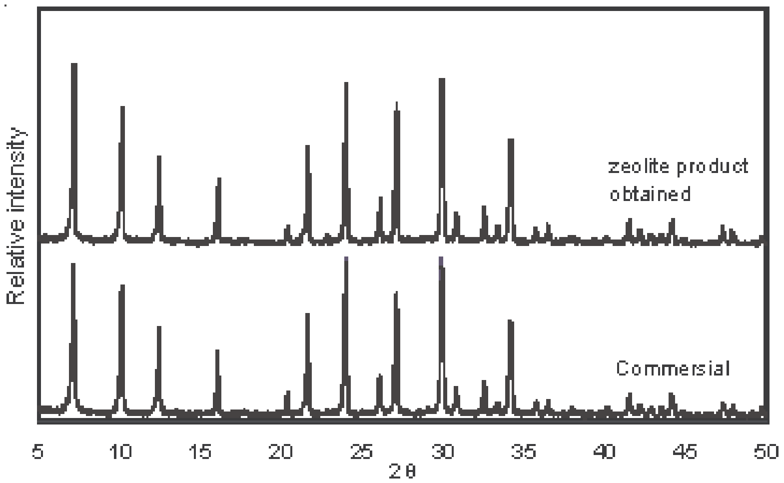

Figure 15. X-ray diffractograms of commercial zeolite and zeolite product obtained using two step method. Reaction condition: 100°C and 5 h

REFERENCES

Akolekar, D., Chaffee, A. and Howe, R.F. 1997, 'The Transformation of Kaolin to Low Silica X Zeolite', *Zeolites*, *vol 19, no. 3*, pp. 359-365.

Alexander, G.B., Heston, W.M., and Iler, R.K. 1954, 'The Solubility of Amorphous Silica in Water', *Journal of Physical chemistry*, *vol. 58, no. 6*, pp. 453-5.

Antonic T., Cizmek A., and Subotic B. 1994, 'Dissolution of Amorphous Aluminosilicate Zeolite Precursors in Alkaline Solutions : Part 2. Mechanism of The Dissolution', *J. Chem. Soc., Faraday Trans*. *Vol. 90, no. 13*, pp. 1973–7.

Antonic T., Cizmek A., Kosanovic, C. and Subotic, B. 1993, 'Dissolution of amorphous aluminosilicate zeolite precursors in alkaline solutions: Part 1. Kinetics of the dissolution', *J. Chem. Soc., Faraday Trans*. *Vol. 89, no. 11*, pp. 1817–1822.

Armbruster T. 2001, 'Clinoptilolite-heulandite: applications and basic research. In : Galarnau A., Di Renzo, F., Faujula. F. and. Vedrine J. (Editors)', *Studies in Surface Science and Catalysis 135: Zeolites and Mesoporous Materials at the Dawn of the 21st Century*, Elsvier Science B.V, pp. 3-17.

ASTM D:5357-98, *Standard Test for Determination of Relative Crystallinity of Zeolite Sodium A by X-Ray Diffraction*.

Basaldella, E.I., Kikot, A., and Pereira, E. 1990, 'Synthesis of Zeolites from Mechanically Activated Kaolin Clays', *Reactivity of Solids*, *vol. 8*, pp. 169-77.

Benning, L.B., Wilkin R.T. and Barnes, H.L. 2000, 'Solubility and Stability of Zeolite in Aueous Solution: II. Calcic clinoptilolite and mordenite', *American Mineralogist*, *vol. 85*, pp. 495-508.

Breck, D.W. 1974, *Zeolite Molecular Sieves: Structure, Chemistry and Use*. John Wiley & Son, New York.

Burriesci, N., Crisafulli, M., Giordano, N. and Antonucci P.L. 1986, 'Iron-free Zeolites from Lipari Pumie', *Zeolites*, *vol.6, no.2*, pp. 119-124.

Cizmek, A., Komunjer, L. and Subotic, B. 1996, 'Kinetics of zeolite dissolution: Part 3. Dissolution of synthetic mordenite in Hot Sodium Hydroxyde Solutions', *Zeolites*, *vol. 12*, pp. 190-6.

de-Lucas, -Antonio, Uguina,- Angeles, M., Covian,-Ignacio 1992, 'Synthesis of 13X Zeolite from Calcined Kaolins and Sodium Silicate for Use in Detergents', *Industrial and*

Engineering Chemistry Research, *vol. 31, Sept*, pp. 2134-40.

Dmitrevskii, G.E., Martynova, L.G., Antoshenko, E.I. and Lukomskaya, Z.T. 1971, 'Solubility of Silica in solutions of Caustic Alkalies and of Sodium And Potassium Carbonate', *Journal of Applied Chemistry*, *vol. 44, no. 11*, pp. 2451-5.

Drag, E.B, Miecznikowski, F., Abo-Lemon and Rutkowshi M. 1985, 'Synthesis of A, X and Y Zeolites from Clay Minerals. B.S. Drazj, Hocevarand and Pejovnovik (Editors)', *Zeolites*, Science Publisher B.V, Amsterdam, pp. 147-154.

Fang, L.C., Cheng, H.H. 1995, 'Resource Recovery of Waste Fly Ash: Synthesis of Zeolite-like Materials', *Environmental Science and Technology*, *29*.

Ghobarkar, H., Schaf, O. and Guth, U. 1999, 'Zeolites-from kitchen to space', *Prog. Solid St. Chem.*, *vol 27*, pp.29-73.

Imbert, F.E., Moreno, C. and Montero 1994, 'Venezuelan Natural Aluminosilicate as a Feedstock in the Synthesis of Zeolite A.', *Zeolites*, *vol. 14, no. 6*, pp. 374-8.

Kang S.J. and Egashira K. 1997, 'Modification of different grades of Korean natural zeolites for increasing cation exchange capacity', *Applied Clay Science vol. 12*, pp.131 – 144.

Lechert, H. and Kacirek, H. 1993, 'The Kinetics of Nucleation of X Zeolites', *Zeolites, vol. 13, March*, pp 192-8.

Leonard J.L. 1981, 'Preparation of Zeolite A by Hydrothermal Treatment of Clinoptilolite', *US Patent No. 4,247,524,27 January.*

Roozeboom, F., Robson, H. E. and Chan, S.S. 1987, *Study on the Mechanism of Zeolites A, X and Y*. pp.127-147 .

Shi, H.N. 1983, 'Two Step Process for the Preparation of Zeolite A by Hydrothermal Treatment of Clinoptilolite', *US Patent No. 4,401,634, 30 August.*

Subotic, B., Skrtic, D. and Smit I. 1980, 'Transformation of Zeolite A into Hydroxysodalite', *Journal of Crystal Growth*, *vol. 50 pp*. 498-508.

Yoshida, A. and Inoue, K. 1988, 'Whiteness in Zeolite A Prepared from Shirazu Volcanic Glass', *Zeolites*, *vol. 8, no. 3*, 94-100.

Yoshida, A. and Inoueo, K. 1986, 'Formation of Faujasite-type Zeolite from Ground Shirazu Volcanic Glass', *Zeolites*, *vol. 6 no. 8, pp*. 467-73.