

PRODUCTION OF NOVEL ZEOLITE OF TYPE Na-P FROM SODIUM ALUMINATE LIQUOR/SPENT LIQUOR/ALUMINA TRI-HYDRATE OF NALCO'S ALUMINA REFINERY, DAMANJODI,ORISSA,INDIA: A UNIQUE MATERIAL FOR DETERGENT FORMULATION

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Abstract

A Process for production of novel synthetic crystalline porous alumino silicate Zeolite Na-P consisting of the oxides of silicon and aluminium represented by the formula $a\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:b\text{SiO}_2$, wherein $a = 0.1-1.0$ and $b = 2.2-5.0$ has been developed from three different raw materials viz. Sodium Aluminate Liquor/Spent Liquor/Alumina Tri-hydrate of NALCO's Alumina Refinery, Damanjodi, Orissa. Zeolite Na-P was produced by preparing a gel by mixing Sodium Silicate, Sodium Aluminate Liquor/Spent Liquor/Alumina Tri-hydrate, autoclaving the gel at 80-150 Degree Celsius for a period of 2 hrs to 4 days under static or stirred condition, quenching the resultant crystalline material in cold water, separating the catalyst formed, washing with water, drying the solid catalyst at a temperature of 80-120 Degree Celsius for a period of 3-12 hrs to obtain the product which can be used as a builder material for detergent formulation.

Introduction

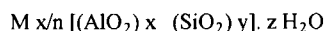
In the past thirty-five years, Zeolites have stimulated a huge amount of academic and industrial research and impacted several adsorption, ion-exchange and catalytic processes. The commercial success of Zeolites was due primarily to their unique structure and composition controlled properties which permitted the improvement of known processes and the development of new ones.

The present work relates to a process for the preparation of novel crystalline aluminosilicate composite material using alumina source materials obtained from the alumina refinery of National Aluminium Company Ltd., Orissa, India. More particularly, this work relates to the preparation of crystalline micro porous aluminosilicate molecular sieve of Zeolite-P type structure exhibiting its suitability for several adsorption, ion-exchange and detergency processes of academic and industrial importance.

Compared to resins, Zeolites have found advantageous application as ion-exchangers in the last thirty years. In general, Zeolites are used where economic considerations or where a high thermal and/or radiation flux exclude the use of resins. Thus, Zeolites find application as water softeners in detergency where the relatively lower cost of Zeolites makes it an attractive option in such a 'throw-away' application or in the removal and storage of radionuclides where the considerable resistance of some Zeolites to radiation and thermal damage make them an obvious choice.

The term 'molecular sieve' was proposed in 1932 by J.W.McBain to describe the selective adsorption of molecules of relatively small size over molecules of larger size by Chabazite, a mineral Zeolite which has been purged free of adsorbed water. Zeolites

are micro porous, crystalline, hydrated aluminosilicate molecular sieves. Structurally, they possess rigid three dimensional framework comprising of $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedral linked through oxygen bridges and enclosing cavities and channels of molecular dimensions. Each $[\text{AlO}_4]$ tetrahedron imparts a negative charge on the framework of Zeolite. The framework negative charge is balanced by cations occupying extra-framework positions. A general formula for a Zeolite can be represented by its unit cell composition as:



Where M represents the exchangeable charge balancing cations usually from group I or II of the Periodic Table, with a valency 'n', x, y and $z > 0$. According to Lowenstein rule, the lower limit for y/x ratio tends to a value 1.0. Therefore, the relationship of aluminium to the charge balancing cations such as La/3, Ca/2, Na, K etc can be expressed as equal to unity. One type of cation may be exchanged either completely or partially with another cation following ion-exchanging techniques in a conventional manner. By means of such cation exchange, it has been possible to vary the properties of a given aluminosilicate by suitable selection of cation.

The reversible cation exchange is one of the important properties of crystalline alumino-silicate zeolites. The isomorphous replacement of Si^{4+} by Al^{3+} is responsible for the creation of a cation exchange site which is usually occupied by Na^+ . Zeolite-A, therefore, being the most aluminium – containing zeolite, offers maximum number of cation exchange sites. Therefore, until recently, Zeolite-A was used in the formulation of laundry-detergents of the non-phosphatic (free from STPP) type. Zeolitic extra-framework sodium cations, by replacing the cations like Mg^{+2} , Ca^{+2} etc. that impart hardness to water, thus renders soft water, easing out the washing action by the removal of dust particles etc.

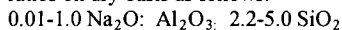
The Hydrothermal Synthesis

Much of the success in the laboratory syntheses has come from the duplication of the conditions that produce natural zeolites. Zeolites are formed under hydrothermal conditions. The term hydrothermal is used in a broad sense and includes the crystallization of zeolites from aqueous system comprising of necessary ingredients. The essential process involved in the hydrothermal synthesis of most of the zeolites, is the conversion of amorphous reactive supersaturated aluminosilicate gels into crystalline ones, in the presence of aqueous solution of alkali and/or alkaline earth metal hydroxide at higher temperature (298-573K). The actual mechanism of zeolite crystallization is not well understood because of the complexity of the interactions

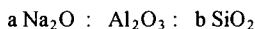
occurring in the hydrothermal magma. The gross composition of reaction mixture contributes to a specific aspect of crystallization. However, there is a substantial interplay between the three variables viz. gross-composition, temperature and time during the course of crystallization.

In recent years, a number of patents have established the fact that Zeolite-P instead of Zeolite-A, is preferred in the formulation of laundry- detergents, perhaps on account of ease and higher rate of cation exchange including higher Magnesium ion-exchange capacity compared to zeolite of type-A. These zeolites will usually have calcium exchange capacity of at least 150mg CaO per gram of anhydrous aluminosilicate. Zeolite-P belongs to a family of small pore zeolites possessing low to intermediate Si/Al ratio (1.1 to 2.5).

The crystalline, porous aluminosilicate of type-P zeolite structure, prepared by the process developed are constituted of oxides of silicon and aluminium having well ordered porous structure consisting of channels of precisely defined and uniform dimensions. The zeolite type Na-P prepared by the process developed has a chemical composition, in terms of oxide mole ratios on dry basis as follows:



Accordingly, the process developed for the preparation of novel synthetic crystalline zeolite of type Na-P consisting of the oxides of silicon and aluminium by the hydrothermal crystallization process having in the mole ratios of oxides in the anhydrous state represented by the formula:



wherein $a = 0.1 - 1.0$ and $b = 2.2 - 5.0$ and characterized by X-Ray Powder Diffraction Data which comprises preparing a gel by mixing a source of silicon, aluminium and sodium, autoclaving the resultant gel at a temperature in the range of 80-150^o C for a period ranging between 2hrs to 4 days under static and/or stirred condition, quenching the resultant crystalline material in cold water, separating the catalyst formed by conventional methods, washing with deionised water thoroughly up to wash water pH is in the range of 9.0 to 11.0, drying the solid catalyst at a temperature in the range of 80-120^oC for a period ranging from 3-12 hrs. to obtain the product.

Table -1 Representative Physical Properties Data for Zeolite-P

Chemical Composition:	
Typical Oxide Formula	: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2-5 \text{ SiO}_2 \cdot 5\text{H}_2\text{O}$
Typical Unit Cell Content	: $\text{Na}_6 [(\text{AlO}_2)_6 (\text{SiO}_2)_{10}] \cdot 15 \text{ H}_2\text{O}$
Variations	: Si/Al = 1.1 to 2.5
Crystallographic Data	
Summity	: Near Cubic
Space Group	: 14/amd
Density	: 2.01g/cc
Unit Cell Volume	: 1015 \AA^3
Unit Cell Constant	: $a = 10.05 \text{ \AA}$
Structural Properties	
Framework	: Same as gismondine
SBU: S4R	Void Volume : 0.41cc/cc
	Framework Density : 1.57 g/cc

Analysis of NALCO Origin Raw Materials

The NALCO origin raw materials viz. Alumina Tri-hydrate, Sodium Aluminate Liquor and Spent Liquors were analyzed and the chemical analyses are presented in Table-2 below.

Table-2 .Chemical Analysis of NALCO Origin Raw Materials

Wt. % ⇔	LOI	Al ₂ O ₃	Na ₂ O	K ₂ O	Fe ₂ O ₃
Material ↓					
Alumina Trihydrate Powder	33.84	65.35	0.66	0.04	0.11
Sodium Aluminate Liquor					
Sample-I	78.68	10.11	11.12	0.086	ND
Sample-II	77.70	9.83	11.70	0.077	ND
Sample-III	79.84	8.19	11.88	0.089	ND
Sample-IV	77.41	1060	11.87	0.089	ND
Spent Liquor					
Sample-I	79.38	6.12	14.50	ND	ND
Sample-II	78.57	6.37	15.06	ND	ND
Sample-III	78.58	6.29	15.13	ND	ND
Sample-IV	78.61	5.94	15.45	ND	ND

ND= Not Detectable

The nature of the raw materials and their treatment prior to the formulation plays an important role in the crystallization process. Attention was focused in the formation of zeolite of type Pc by reproducible, economical processes and by utilizing mildest possible conditions. The concentration of reacting components in the initial gel formation is one of the major factors in determining the species produced. Accordingly, attempts were made to develop a process for crystallization of zeolite-P using NALCO based raw materials.

Preparation of Zeolite -P using NALCO origin Sodium Aluminate Liquor

(A)Laboratory Scale Studies:

The analysis of Sodium Aluminate Liquor showed that the Na₂O content was 11.5±0.4 whereas % Al₂O₃ was ranging from 8.19 to 10.60. The variation in the alumina content may be due to settling down of alumina during transport of sample and ageing. Since Na₂O content is high, the gel composition from which Zeolite-P was crystallized using synthetic Sodium Aluminate viz. 2.58Na₂O:Al₂O₃:3.8SiO₂:94H₂O was found to be unsuitable for preparation of Zeolite-P using NALCO origin Sodium Aluminate Liquor. Na₂O/SiO₂, H₂O/Na₂O ratios and nature of the raw material were found to be the influencing synthesis parameters, different compositions were examined on the basis of the earlier results. Each composition was again subjected to different hydrothermal conditions for crystallization. However, after optimizing gel composition, a part of the investigation is

summarized in Table-3 indicating the complexity in optimizing the synthesis conditions using NALCO origin Sodium Aluminate Liquor as a source of aluminium. The gel composition was chosen as $4.39\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:3.56\text{SiO}_2:225\text{H}_2\text{O}$. NALCO origin Sodium Aluminate Liquor from Sample-I was used as a source of aluminium. For silica source, Sodium Silicate (28%SiO₂, 8.5%Na₂O) was used for the gel preparation. In a gel preparation, 15ml water was added to 14.98 g of Sodium Silicate and stirred for 10 minutes. To this was added a solution of 20.18 g Sodium Aluminate diluted with 20ml of water with constant stirring for 10 min. 2.48g NaOH in 21ml of water was added to the above resultant mixture with constant stirring for 15 minutes. The resultant gel was further stirred for about 30 minutes. The homogeneous gel so formed was then transferred to the stainless steel autoclave. For each experiment, starting gel was prepared freshly with the same composition and then subjected to the desired hydrothermal treatment as tabulated in Table-3. After the autoclave attained the desired temperature, the time was recorded as the zeroth hour. The heat-up time varied for the different temperatures. The heat-up time was estimated as the time needed to attain the set temperature of the oven in the reactor after keeping it in the oven. The autoclaves were quenched to room temperature and solid product was separated by suction filtration. Sufficient washing of the wet cake with distilled water was ensured by checking pH of the filtrate and colour of the solid product. The product was dried at 120°C for 4 hrs.

Physico-chemical Characterization: The pure, crystalline Na-P type zeolite obtained from Batch No. 11 of Table-3 was characterized by powder X-ray diffraction, Infrared Spectroscopy, Scanning Electron Microscopy, Chemical Analysis by Atomic Absorption Spectroscopy and X-Ray Fluorescence techniques, Calcium Exchange Capacity and Whiteness Index.

Table-3. Crystallization of Zeolite of type-P using NALCO Sodium Aluminate Liquor as a Source of Aluminium.

Batch No.	Aging Temp.(°C)	Period (hrs.)	Crystallization Temp.(°C)	Period (hrs.)
1	-	-	85	9
2	-	-	100	24
3	-	-	110	12
4	-	-	120	6
5	-	-	120	8
6	-	-	120	16
7	-	-	120	24
8	100	12	110	2
9	100	12	110	4
10	100	12	110	6
11	100	12	110	8
12	100	12	110	10
13	100	12	110	12
14	100	16	110	16
15	100	16	110	25

Chemical Analysis: (Si/Al)_{Chem. Anal.} = 1.52, (Si/Al)_{XRF} = 1.49
 Calcium Exchange Capacity: 169.4mgCaO per 1 gm of anhydrous Zeolite-P. Whiteness Index: 95(with respect to) BaSO₄).

(B) Scaling Up:

Based on the above results, an attempt was also made for scaling up by using autoclave of 20 l capacity equipped with open turbine type agitator. The oxide mole composition in the initial gel

mixture used in the scaling-up runs was $4.24\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:3.56\text{SiO}_2:225\text{H}_2\text{O}$. In the first scaled-up batch, the quantities weighed and mixing sequence followed were as follows.

2 l of distilled water was added to 1.526 Kg of Sodium Silicate and stirred for 10 minutes. To this was added a solution of 2.018Kg of Sodium Aluminate Liquor of NALCO origin diluted with 1 l of distilled water with constant stirring for 15 minutes. 0.222Kg of NaOH pellets were dissolved in 1.5 l of distilled water and it was added to the above resultant solution with constant stirring for 15 minutes. The formed gel was further stirred for about 2 hrs and then this homogeneous gel was transferred to an autoclave of 20 l capacity. The temperature was raised using the following programme.

- Room Temp. to 50° C : time taken - 1hr 15min.
- 50° C -75° C : time taken- 30min.
- 75° C – 100° C : time taken -30min and allowed to age for 12hrs.
- 100° C – 110° C : time taken – 45 min. and allowed to crystallize for 8 hrs.

In order to check the progressive crystallization of desired phase, samples were removed after different length of crystallization period viz. 5hr, 6hr 30 min and 8 hr and they were examined by XRD after filtration, washing and drying. After confirming the purity and crystallinity to maximum extent, the product was drained out after cooling the autoclave to room temperature. Product was separated by suction filtration and washed by distilled water till the effluent showed pH in the range of 9.5 – 10.5. Solid was dried at 110°C for at least 4 hrs. The dried product was characterized by XRD, XRF, SEM and for Whiteness Index and Calcium Exchange Capacity. These results are shown in Table-4 along with the characteristics of the products obtained from the next scaled-up processes from batch –II to batch-IV. The quantities of raw materials used for scaling up the process for different batches are summarized in Table- 5.

Table-4.Characteristics of the Products Zeolite-P obtained from the Scaled-up batches

Analysis	Batch-I	Batch-II	Batch-III	Batch-IV
Chemical Analysis (Si/Al) _{chem. anal.}	1.48	1.52	1.50	1.49
(Si/Al) _{XRF}	1.47	1.49	1.52	1.47
Calcium Exchange Capacity mg of CaO/g(anhyd.)	170	170	163	171
Whiteness Index (w.r.to BaSO ₄)	96	95	95	96

Table-5.Quantities of Raw Materials used for Scaling-up the Process

Batch No.	Sodium Silicate (kgs)	Sodium Aluminate Liquor (k gs)	NaOH (kgs)	Total H ₂ O (Lit.)
1	1.526	2.018	0.222	5.5
2	2.289	3.027	0.333	8.25
3	3.052	4.036	0.444	11.0
4	3.052	4.036	0.444	11.0

Preparation of Zeolite of type P using NALCO origin Alumina Tri-hydrate (ATH) Powder

(A) Laboratory Scale Studies:

Experiments were conducted without any prior treatment for the dissolution of ATH in order to seek the possibility of reducing this additional step during the synthesis and thereby energy consumption.

Table-6. Details of Synthesis runs using NALCO based ATH

Batch No.	Oxide Mole Composition	Crystallization		XRD
		Time	Period	
1	2.4Na ₂ O:Al ₂ O ₃ :3.87SiO ₂ :145H ₂ O	110°C	8hrs.	HS
2	2.4Na ₂ O:Al ₂ O ₃ :3.87SiO ₂ :145H ₂ O	120°C	8hrs.	Unknown phase
3	2.4Na ₂ O:Al ₂ O ₃ :3.87SiO ₂ :145H ₂ O	105°C	8hrs.	Pc+Unknown phase
4	2.4Na ₂ O:Al ₂ O ₃ :3.87SiO ₂ :145H ₂ O	85°C	8hrs.	Unknown phase
5	2.4Na ₂ O:Al ₂ O ₃ :3.87SiO ₂ :145H ₂ O	1100C	12hrs	Unknown phase
6	3.9Na ₂ O:Al ₂ O ₃ :2.42SiO ₂ :154H ₂ O	110°C 120°C	12hrs 24hrs	HS
7	4.22Na ₂ O:Al ₂ O ₃ :3.87SiO ₂ :145H ₂ O	110°C	8hrs.	Pc+ analcime
8	4.22Na ₂ O:Al ₂ O ₃ :3.87SiO ₂ :145H ₂ O	120°C	12hrs	HS
9	5.17Na ₂ O:Al ₂ O ₃ :3.87SiO ₂ :145H ₂ O	120°C	12hrs	Pc+HS
10	2.76Na ₂ O:Al ₂ O ₃ :1.91SiO ₂ :170H ₂ O	120°C	8hrs.	HS
11	3.75Na ₂ O:Al ₂ O ₃ :3.5SiO ₂ :160H ₂ O	1200C	40hrs	Mix phase
12	4.24Na ₂ O:Al ₂ O ₃ :3.56SiO ₂ :225H ₂ O	100°C 110°C	12hrs 6hrs.	Mix phase
13	8Na ₂ O:Al ₂ O ₃ :6.7SiO ₂ :344H ₂ O	100°C 110°C	12hrs 6hrs	Pc+ analcime
14	8Na ₂ O:Al ₂ O ₃ :6.7SiO ₂ :344H ₂ O	120°C	17hrs	Pc+ analcime

In the typical gel preparation using composition-1 from Table- 6, 16.28g of sodium silicate was diluted with 10ml of distilled water and kept under mechanical stirring. 3.12g alumina tri-hydrate powder of NALCO origin (65.35%Al₂O₃) was mixed with 2.1g of NaOH (96% Ranbaxy) & 30ml of distilled water. This mixture was then added in to Na₂SiO₃ solution slowly. The resultant mixture was then stirred further for 30min. and then transferred to a Teflon lined stainless steel lined autoclave. This autoclave was then subjected to the hydrothermal treatment in an air oven and temperature was raised stepwise to 110°C. It was allowed to crystallize for a period of 8hrs. After 8hrs., autoclave was quenched, product was filtered, washed thoroughly to remove excess Na₂O and then dried in an oven at 110°C for 6 hrs. XRD profile of this product confirms the presence of HS phase. Similarly, without dissolution of ATH, different compositions at different reaction parameters yielded other than pure Na-Pc phase. Some unidentified phases, HS, analcime, etc. have been formed predominantly in the pure form or in the major contribution as a result of using as- supplied form of ATH from the alumina refinery plant of NALCO. Therefore, it was decided to conduct

the experiments with prior treatment of dissolution of as- supplied form of ATH.

Further attempts were made to optimize synthesis conditions including the oxide mole compositions which will yield pure crystalline Na-P with reasonably good reproducibility. Following compositions gave the satisfactory results.

- 4.24Na₂O:Al₂O₃:3.56SiO₂:225H₂O ----- (1)
2.76Na₂O:Al₂O₃:1.91SiO₂:170H₂O----- (2)

Scaling –up:

For the dissolution of ATH using composition (1), 352 g of ATH was mixed with a solution of 578g of NaOH dissolved in 3 l of distilled water. This solution of ATH was then heated in a S.S. autoclave of 20 l capacity followed by increasing the temperature up to 120°C and examined the extent of dissolution at 6,8,12,16,18,24, 36 & 48hrs. Instead of increasing temperature for the complete dissolution increase in the strength of alkali solution was preferred by decreasing the quantity of water by 50%. Same set of experiments were carried out at 120°C for different length of period. After 16 hrs. a clear solution of ATH was obtained indicating complete dissolution. This solution was then discharged and water loss was adjusted by adding required amount of distilled water. 1.686Kg sodium silicate was diluted with 5.3 l of distilled water with constant stirring. Clear solution of ATH was then added slowly under vigorous stirring to the diluted sodium silicate solution. The gel mixture formed was further stirred for 2hrs. until the gel becomes homogenous. It was then transferred to an autoclave of 20 l capacity with the help of addl. one liter of distilled water. The autoclave was then heated to 100°C by stepwise increment viz. (a) from room temp. to 50°C, (b) from 50°C to 100°C and hold for 12hrs. Then the temperature was further increased from 100°C to 110°C. After 6 hrs cooling was started under normal condition and then the product was discharged along with the mother liquor. Product was separated by vacuum filtration followed by washing till effluent showed pH in between 9-11. Product was dried in an air oven at 120°C for 4 hrs. XRD profile showed pure and well crystalline Na-Pc phase. Using composition(2), another scale up experiment was carried out in the similar way as above and XRD profile showed pure and well crystalline Na-Pc phase. Comparative details of above scaled –up representative batches are summarized in Table-7.

Table-7. Comparative studies of scaled -up batches using different compositions

Batch Composition	Weight(Kg) raw material taken				Crystallization Temp./Time	Yield (g)	Product Si/Al XRF
	Sod. Silicate	ATH	NaOH	H2O			
(1)	1.686	0.352	0.578	7.800	100°C/ 12h	759	1.39
					110°C/ 6h		
(2)	1.206	0.473	0.530	8.139	120°C/8h	501	1.51

Table-8. The physico-chemical characterization of the products

Analysis	Composition(1)	Composition(2)
Chemical Analysis (Si/Al) _{chemical analysis} (Si/Al) _{XRF}	1.38 1.39	1.44 1.51
Calcium Exchange Capacity Mg of CaO/g(anhyd.)	163	160
% Whiteness Index (w.r.to BaSO ₄)	94	94

Preparation of Zeolite-P using NALCO origin Spent Liquor

(A) Laboratory Scale Studies:

For undertaking laboratory scale study, following two modified compositions were tried for hydrothermal crystallization for preparation of Zeolite-P using NALCO origin Spent Liquor.

- (a) 4.98Na₂O:Al₂O₃:1.91SiO₂:170H₂O
 (b) 4.98Na₂O:Al₂O₃:3.56SiO₂:225H₂O

Studies were conducted for increasing the SiO₂/Al₂O₃ mole ratio in the gel mixture by reducing the alumina content. However, with the change in quantity of alumina, the change in Na₂O content was made in such a way that they fall in proper range H₂O/Na₂O and Na₂O/SiO₂ mole ratios favorable to yield Na-P phase. Experiments with reducing alumina moles systematically from 1.0 mole to 0.75 moles, 0.7 moles, 0.6 moles and to 0.5 moles were conducted. Table-9 summarizes the runs carried out at different temperature and period.

Table-9. Laboratory scale runs using spent liquor

Batch No.	Molar SiO ₂ /Al ₂ O ₃ in gel mixture	Crystallization Temp./Period	Phase Identification (XRD)
1	3.56	120 ^o C/8hrs.	X +A+HS
2	4.75	120 ^o C/8hrs.	X+Na-Pc traces
3	5.33	100 ^o C/12hrs. 110 ^o C/6hrs.	X+Na-Pc traces
4	5.33	120 ^o C/8hrs.	X+Na-Pc traces
5.	7.11	120 ^o C/8hrs.	Na-Pc
6	7.11	120 ^o C/8hrs.	Na-Pc
7	7.11	100 ^o C/12hrs. 110 ^o /6hrs.	Na-Pc

It is evident from the Table-9 that pure Na-Pc was crystallized with only SiO₂/Al₂O₃ ratio equal to 7.11. The composition 6.66 Na₂O:Al₂O₃:7.11SiO₂:448H₂O was further examined with reducing water content in order to reduce the batch volume. Unfortunately, H₂O/Na₂O molar ratio below 67.27 failed to form Zeolite-P phase in present studies keeping SiO₂/Al₂O₃=7.11 and Na₂O/SiO₂ ratio=0.936. In a typical gel preparation, 22.44 g of sodium silicate was diluted with 45 ml of distilled water and kept under stirring for 15 mins. 24.03 g of spent liquor diluted with 43ml of H₂O was added slowly in to the above solution for 20 min. under vigorous stirring. The gel mixture formed was then further stirred for 30 min. for homogeneity. This gel mixture was then transferred to Teflon lined S.S. autoclave which was then

subjected to an oven at 120^oC for 8hrs. The temperature 120^oC was achieved stepwise in order to avoid shooting up of the desired temperature. Kinetics of crystallization using this composition was studied by preparing fresh gel for each batch and quenched after 2, 4,6,8,10,12 & 16 hrs. After quenching autoclave, product was filtered and washed with distilled water. The wet cake of the product was then dried in an oven at 120^oC for 6 hrs. XRD profile of the product obtained after 8 hrs showed the most pure and fully crystalline Na-Pc phase. Further, the effect of ageing was also examined for the final Si/Al ratio in the product and morphology. As there was only marginal difference in the both, the batch with less crystallization time was preferred for the scaling up studies.

(B) Scaling up:

For scaling up, autoclaves of 20 l, 50 l and 500 l capacity equipped with open turbine type agitator were used for batches A, B and C respectively and summarized in Table 10 and 11.

Table-10. Step-wise scaling up using NALCO Spent Liquor

Batch No.	Weights(Kg) of raw materials taken			Yield(g)	Crystallinity (%)	Si/Al (XRD)
	Sodium silicate	Spent Liq.	Water			
A	2.244	2.403	8.8	702	93	1.69
B	6.760	7.209	26.4	2020	95	1.70
C	58.63	63.15	227.0	18,440	97	1.69

Table-11. The physico-chemical characterization of the final products obtained from the above three scaled-up batches.

Analysis	Batch-A	Batch-B	Batch-C
Chemical Analysis (Si/Al) _{chem. analysis} (Si/Al) _{XRF}	1.69 1.68	1.71 1.69	1.68 1.70
Calcium Exchange Capacity Mg of CaO/g(anhyd.)	162	160	161
% Whiteness Index (w.r.to BaSO ₄)	96	96	96

Conclusion

Results of the above laboratory and scale-up studies indicated that Zeolite-P can be produced from NALCO origin raw materials viz. Sodium Aluminate Liquor/Alumina Trihydrate/Spent Liquor which can be used as a builder material in detergent formulation having better efficiency than detergent grade Zeolite-A.

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References

1. R.A.Llenado, Proceedings of 6th International Zeolite Conference, Reno, USA (Butterworth, 1984), pp.940.
2. J.D.Sherman, Zeolites: Science and Technology, NATO ASI Ser. E: Applied Sciences No. 80, 1984, pp.583.
3. D.W. Breck, Zeolites Molecular Sieves, J.Wiley and Sons. New York, 1974.
4. R.M. Milton, US Patent 2,882,243 and 2,882,244(1959).
5. D.W. Breck, and E.M. Flanigen,, Molecular Sieves, Soc. Chem. Ind., London, 1968, pp.47.
6. D.W Breck., US Patent, 3,054,657(1962).
7. R.M. Milton, US Patent, 3,030,181(1962), Brit. Patent., 841,812(1960).
8. D.W. Breck, US Patent, 3,130,007(1964).
9. L.V.C. Rees and S.Chandrasekhar, Zeolites, 1993, 13, pp, 534.
10. PCT Int. Appl. WO 94 26,662(1994).
11. PCT Intl. Appl. WO 95 12, 546(1995).
12. Japan Kokai Tokkyo Koho JP, 02,173, 094 (1990).
13. Japan Kokai Tokkyo Koho JP 05,238,724 (1993).
14. H. Robson, Chemtech, March, 1978.