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(72) Araya, Abraham, GB

(73) Crosfield Limited, GB

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(54) **ALUMINOSILICATES**

(54) **PROCESS FOR MAKING ZEOLITE P**

(57) On mélange du silicate de sodium, de l'aluminate de sodium et de la soude caustique de manière à produire un gel de la formule générale suivante: $2,5-7,5 \text{ Na}_2\text{O}$, $2,2-3,0 \text{ SiO}_2 \cdot \text{Al}_2\text{O}_3$, $80-250 \text{ H}_2\text{O}$ et un volume de plus de $1,5\text{m}^3$, aucune zéolite A n'étant détectée aux rayons X et sans adjonction de zéolite P, le produit obtenu étant ensuite filtré, lavé et séché. On peut également produire à échelle industrielle un aluminosilicate de métal alcalin de type zéolite P représenté par la formule d'oxyde $\text{M}_{2n} \cdot \text{Al}_2\text{O}_3 \cdot 2,0-2,66 \text{ SiO}_2 \cdot y \text{ H}_2\text{O}$.

(57) Sodium silicate, sodium aluminate and sodium hydroxide are mixed together to produce a gel having the general formula: $2.5-7.5 \text{ Na}_2\text{O}$, $2.2-3.0 \text{ SiO}_2 \cdot \text{Al}_2\text{O}_3$, $80-250 \text{ H}_2\text{O}$ and a volume of more than 1.5 m^3 , no XRD detectable zeolite A being produced and no zeolite P being added, the product being eventually filtered washed and dried. It is thus possible to produce on an industrial scale an alkali metal aluminosilicate of zeolite P type having the oxide formula: $\text{M}_{2n} \cdot \text{Al}_2\text{O}_3 \cdot 2.0-2.6 \text{ SiO}_2 \cdot y \text{ H}_2\text{O}$.

ABSTRACT

Sodium silicate, sodium aluminate and sodium hydroxide are mixed together to produce a gel having the general
5 formula:

2.5-7.5 Na₂O, 2.2-3.0 SiO₂, Al₂O₃, 80-250 H₂O
and a volume of more than 1.5 m³, no XRD detectable
zeolite A being produced and no zeolite P being added,
the product being eventually filtered washed and dried.
10 It is thus possible to produce on an industrial scale
an alkali metal aluminosilicate of zeolite P type
having the oxide formula:



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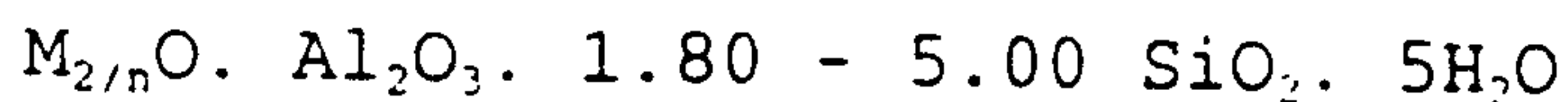
PROCESS FOR MAKING ZEOLITE PField of the Invention

5 The invention describes the preparation of alkali metal
aluminosilicates, in particular crystalline aluminosilicates
having the P-structure. These materials are of value as a
component in detergent formulations in which they remove
calcium and magnesium hardness ions by ion exchange. They
10 also have other properties which provide additional benefits
when used in detergent formulations. These aluminosilicates
will be referred to as zeolite P in this description.

Background of the Invention

15 While the utility of zeolite P in detergent formulations has
been acknowledged, for example in European Patent
Application 0384070 (Unilever), they must be manufactured by
a commercially effective process in order to become
20 available on the market place. Thus, while the properties
of a material may make it a useful commercial commodity, its
manufacture has to be optimised for large scale production.

25 The zeolite P class includes a series of synthetic zeolite
phases which may be in cubic configuration (also termed B or
P_c) or tetragonal configuration (also termed P_t) but is not
limited to these forms. The structure and characteristics
of the zeolite P class are given in "Zeolite Molecular
Sieves" of Donald W Breck (published 1974 and 1984 by Robert
30 E Krieger of Florida USA). The zeolite P class has the
typical oxide formula:



M is an n-valent cation which for this invention is an alkali metal, that is lithium, potassium, sodium, caesium or rubidium with sodium and potassium being preferred and sodium being the cation normally used in commercial processes.

Thus sodium may be present as the major cation with another alkali metal present in a minor proportion to provide a specific benefit.

In EP-A-384,070 is disclosed a process for manufacturing zeolite P having a silicon to aluminium molar ratio not exceeding 1.33 wherein a sodium aluminate solution, having a $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$ molar ratio from 1.4 to 2.0, is mixed with a sodium silicate solution, having a $\text{SiO}_2:\text{Na}_2\text{O}$ molar ratio from 0.8 to 3.4, at a temperature from 25°C to boiling point and with vigorous stirring to give a gel having the following composition:

(2.3-7.5) Na_2O , (1.75-3.5) SiO_2 , Al_2O_3 , (80-450) H_2O .

The gel is then aged for 0.5 to 10 hours at a temperature above 70°C , the crystalline sodium aluminosilicate thus formed being then washed and dried.

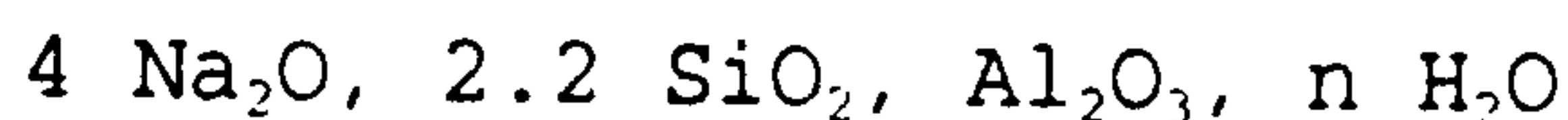
This process, with such a gel composition, even though being suitable for producing zeolite P on a bench scale, can't always be directly transposed to industrial scale.

For some industrial applications requiring large volume production, such as for detergents applications, an industrial scale is defined by a series of compulsory conditions most of them relating to the fact that no batch production process is economic if run in a reactor of less than 2m^3 (i.e a gel volume of about 1.5m^3).

Another parameter, essential in any industrial process, is the yield of the reaction. The yield can be defined as the ratio (mass of zeolite (on dry basis)/mass of reagents). Therefore for a typical zeolite P of the formula:



obtained for example from a gel having the following composition:



the yield can be calculated as follows

$$\begin{aligned} \text{Yield} &= (62 + 120 + 102) / (248 + 132 + 102 + n * 18) \\ &= 284 / (482 + 18 * n) \end{aligned}$$

Thus the limiting factor is the water content of the gel, i.e the dilution. In order to achieve an economical yield, it is therefore not reasonable to work with a too high dilution. Typically n must be below 250. The first limiting factor is therefore the dilution of the gel and it has now been found that everything else being equal, depending only on the dilution it is possible to produce zeolite P or zeolite A or a mixture thereof.

Another parameter also directly related to the size of the reactor is the mixing of the sodium aluminate and sodium silicate solutions and the stirring of the resulting solution.

The mixing can be defined by the order of addition (e.g. the sodium aluminate added in a pool of sodium silicate or vice versa, or simultaneous addition of both reactants in a batch reactor) and the rate of addition. It takes obviously longer

to add 1000 litres in a pool of 1000 litres than to add 1
litre in a pool of 1 litre and it has now been found that
for a given gel composition, once the mixing of the two
solutions has been completed, depending on the mixing and
stirring conditions anyone of pure zeolite P, a mixture of
zeolite P and zeolite A or pure zeolite A can be obtained.
One of the problems is that the vigorous stirring which can
be achieved on a bench scale, and which allows the formation
of zeolite P instead of zeolite A, can't always be achieved
when stirring a 1.5m³ pool, or bigger. A second limiting
factor is therefore the limited stirring efficiency which
can be achieved in a large-size reactor.

Keeping in mind the two above-mentioned parameters (dilution
and mixing/stirring) it has now been found that it is in any
case impossible to produce pure zeolite P with a gel
dilution n below 250 for a SiO₂/Al₂O₃ molar ratio of the gel
below 2.1 if the gel has a volume of above 1.5m³.

Now it has been found that, if zeolite A is produced
together with zeolite P, the characteristics of the zeolite
P (in term of Calcium uptake rate and Calcium binding
capacity) are not significantly better than those of zeolite
A. The presence of Zeolite A can be detected by XRD.

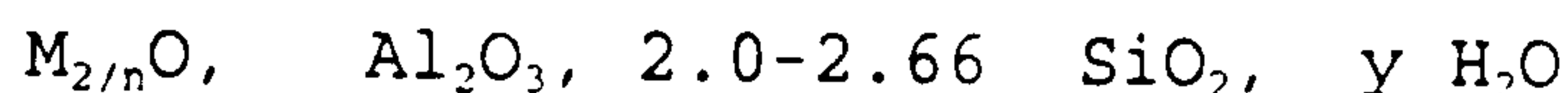
Therefore if a Zeolite P of good quality is to be obtained
by mixing sodium silicate, sodium aluminate, one of the
essential features of the process is that no zeolite A be
produced.

There is therefore a need for a process allowing the
production of good quality zeolite P in pools of more than
1.5m³.

The present invention provides a process for preparing crystalline P-zeolites having $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of less than 2.66.

5 General Description of the Invention

It is an object of the present invention to provide a process for manufacturing an alkali metal aluminosilicate of zeolite P type having the oxide formula



y being the water content, wherein sodium silicate, sodium aluminate and sodium hydroxide are mixed together to produce a gel having the general formula:



and a volume of more than 1.5m^3 ,

20 no XRD detectable zeolite A being produced and no zeolite P being added, the product being eventually filtered washed and dried.

25 Standard Procedures

In the characterisation of the zeolite-P materials prepared by the present process the following methods were used.

- 30 i. Average Particle size (APS): The average particle size (microns) was measured by a Malvern Mastersizer (Trade Mark) obtainable from Malvern Instruments, England and expressed as the d_{50} , i.e. 50% by weight of the particles have a diameter smaller than the diameter
- 35 quoted. The definitions d_{80} and d_{90} may also be used in

association with the appropriate figure. Prior to measuring the particle size, the sample is dried as a thin layer (about 1.5 mm) at 110°C for two hours in a fan oven.

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ii. Calcium uptake rate (CUR): The rate of removal of Ca^{++} ions from a wash liquor is an important characteristic of a detergency builder. The time, in seconds, is determined for a zeolite, at a concentration of 1.48gdm^{-3} and a temperature of 25°C, to reduce the calcium ion concentration in a 0.01M sodium chloride solution from an initial value of $2 \times 10^{-3}\text{M}$ to 10^{-5}M . The zeolite was first equilibrated to constant weight over saturated sodium chloride solution and the water content measured.

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iii. Calcium effective binding capacity (CEBC): The CEBC was measured in the presence of a background electrolyte to provide a realistic indicator of calcium ion uptake in a wash liquor environment. A sample of each zeolite was first equilibrated to constant weight over saturated sodium chloride solution and the water content measured. Each equilibrated sample was dispersed in water (1cm^3) in an amount corresponding to 1g dm^{-3} (dry), and the resulting dispersion (1cm^3) was injected into a stirred solution, consisting of 0.01M NaCl solution (50cm^3) and 0.05M CaCl_2 (3.923cm^3), therefore producing a solution of total volume 54.923cm^3 . This corresponded to a concentration of 200 mg CaO per litre, i.e. just greater than the theoretical maximum amount (197 mg) that can be taken up by a zeolite of Si:Al ratio 1.00. The change in Ca^{2+} ion concentration was measured by using a Ca^{2+} ion selective electrode, the final reading being taken after 15 minutes. The temperature was maintained at 25°C

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throughout. The Ca^{2+} ion concentration measured was subtracted from the initial concentration, to give the effective calcium binding capacity of the zeolite sample as mg CaO/g zeolite.

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iv. Oil absorption (OA): This was determined by the ASTM spatula rub-out method (American Standards of Test Materials D281). The test is based on the principle of mixing linseed oil with the particulate zeolite by rubbing with a spatula on a smooth surface until a stiff putty like paste is formed which will not break or separate when it is cut with the spatula. The weight of oil used is then put into the equation:

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In order to measure the oil absorption of the product, the washed filter cakes obtained after crystallisation were merely dried at room temperature as a thin layer of about 2mm until a solids content of at least 78% by weight was achieved, normally this was achieved in 2-3 days.

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v. The form of the zeolite which was produced was established using standard XRD method.

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Specific Description of the Invention

Examples of processes of the invention will now be given to illustrate but not limit the invention.

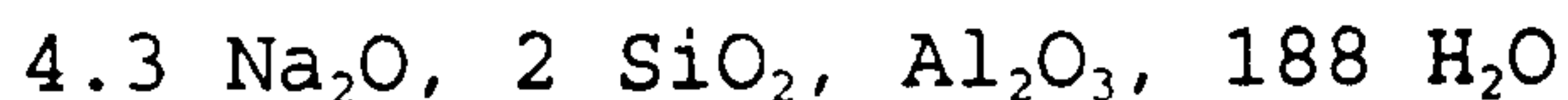
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Example 1

This example illustrates the influence of stirring on zeolite formation.

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A reaction gel with a molar oxide composition of



5 was prepared as follows:

1600 g of 2M sodium hydroxide solution and 517g of commercial sodium aluminate solution (20% Na_2O , 20% Al_2O_3) were placed in a five litre baffled flask connected to a
10 reflux condenser. The resultant solution was then stirred and heated to 90°C.

431g of commercial sodium silicate solution (28.3% SiO_2 , 13.8% Na_2O) was diluted with 1362 g of deionized water. The
15 diluted silicate solution was heated to 75°C and added to the stirred aluminate caustic solution. The resultant reaction mixture gel was allowed to react at 90°C with stirring for 5 hours. The product was then filtered, washed and dried.

20 A first sample was produced with a stirring speed of 500 rpm, the silicate solution being added to the stirred aluminate caustic solution over 20 minutes, this stirring speed and this addition time being considered to be
25 representative of the stirring conditions and addition time which can be achieved at an industrial scale. Zeolite A was produced.

A second sample, using a 1-litre gel having the same
30 composition as in first sample, was produced with a stirring speed of 1200 rpm and an addition of below 5 minutes. Zeolite P was produced.

A third sample was produced using a 1.5m³ gel, in a 2m³
35 vessel, with suitable increased quantities of reactants in

order to produce a gel having the same composition as above
(i.e. $4.3 \text{ Na}_2\text{O}$, 2 SiO_2 , Al_2O_3 , $188 \text{ H}_2\text{O}$).

5 The resultant gel was stirred at 120 rpm, the silicate
solution being added to the stirred aluminate caustic
solution over 20 minutes. Zeolite A was produced.

10 It is therefore proven that, only depending on addition time
and stirring speed it is possible to produce zeolite A or
zeolite P. Since the required conditions (stirring and
addition) to produce zeolite P on a bench scale (2 litres)
can't always be achieved on an industrial scale (gel of
above 1.5m^3) it is necessary to find the gel composition
which allows the formation of zeolite P on an industrial
15 scale.

Example 2

20 Different samples were produced in a 5 litre baffled flask
as disclosed in example 1, the stirring speed being 500rpm
and the silicate solution being added to the stirred
aluminate caustic solution over 20 minutes.

25 The results are summarized in the following Table 1 which
disclosed the gel molar composition as well as the type of
zeolite which has been produced (A, P, A and P) and the
yield of the manufacturing process.

Table 1

Sample	SiO ₂	Al ₂ O ₃	Na ₂ O	H ₂ O	Type of zeolite	Yield (%)
1	2.1	1	4.4	188	A+P	7.5
2	2.1	1	4.1	125	A+Trace P	10.5
3	2.1	1	3.8	100	A	12.4
4	2.2	1	4.4	188	P	7.5
5	2.2	1	4.1	125	P	10.5
6	2.2	1	3.4	75	A	16
7	2.4	1	4.4	188	P	7.4
8	2.4	1	4.4	150	P	9.0
9	2.4	1	4.1	125	P	10.4
10	2.4	1	3.8	100	P	12.3
11	2.4	1	3.4	75	P+A	15.9
12	2.7	1	4.4	188	P	7.5
13	2.7	1	4.4	150	P	10.6
14	2.7	1	3.8	100	P	12.5

It is immediately apparent that using the stirring and addition conditions which prevail on an industrial scale, it is not possible to produce pure zeolite P from a gel composition having a SiO₂/Al₂O₃ molar ratio of 2.1. It is also apparent that, for a given SiO₂/Al₂O₃ gel molar ratio, the higher is the dilution, the easier it is to produce zeolite P.

Nevertheless, it is not enough to produce zeolite P, this zeolite must exhibit good characteristics, particularly in term of Calcium Uptake Rate (CUR in seconds), Calcium Effective Binding Capacity (CEBC in mg/g), Oil Absorption (OA in g oil/ 100g zeolite). These characteristics of the zeolites which have been produced, together with their average particle size (in μm) and their $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio, are summarized in the following Table 2.

Table 2

Sample	$\text{SiO}_2/\text{Al}_2\text{O}_3$	APS	CUR	CEBC	OA
1	2.07	5	80	145	70
2	2.07	6	107	135	65
3	2.07	7	>200	130	60
4	2.10	0.9	8	160	90
5	2.10	1.0	10	158	89
6	2.10	6	>200	135	60
7	2.15	0.85	7	160	92
8	2.15	0.90	6	159	89
9	2.15	1.0	8	160	88
10	2.15	1.2	11	157	85
11	2.15	5	120	140	68
12	2.25	0.90	7	158	89
13	2.25	0.95	8	156	91
14	2.25	0.90	7	155	90

Looking at samples 1 and 11 it can be noticed that, even though zeolite P is produced, the presence of trace of zeolite A is sufficient to significantly reduce the characteristics of the obtained zeolite P. In order to obtain a good quality zeolite P it is therefore essential that no XRD detectable zeolite A be produced.

Example 3

This example illustrates that it is completely possible to produce zeolite P on an industrial scale in a batch process.

A 1.5m³ gel having the following composition:

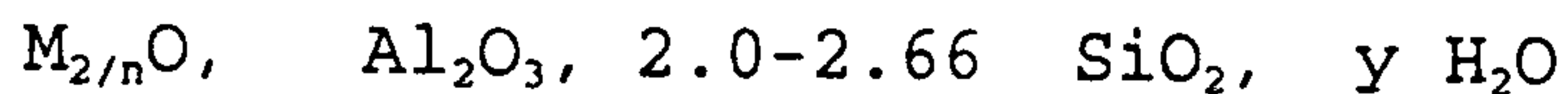
4.5 Na₂O, 2.4 SiO₂, Al₂O₃, 188 H₂O

was produced according to the process disclosed in Example 1, third sample. Pure zeolite P was produced.

A 20m³ gel having the same composition was produced according to the process disclosed in Example 1, third sample, with suitable increase in quantities of reactants. Pure zeolite P was produced.

CLAIMS

1. Process for manufacturing an alkali metal
aluminosilicate of zeolite P type having the oxide
formula



y being the water content, wherein sodium silicate,
sodium aluminate and sodium hydroxide are mixed
together to produce a gel having the general formula:



and a volume of more than 1.5m³,

no XRD detectable zeolite A being produced and no
zeolite P being added, the product being eventually
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