Introduction

PQ Corporation is a leading producer of specialty inorganic chemicals, catalysts and engineered glass products. The Company conducts operations through three principal businesses, the Performance Chemicals division, which develops, manufactures and sells high performance silicate-based specialty chemicals, the Catalysts Division, a leading producer of catalysts and the Potters Division, which manufactures and sells highly engineered solids and hollow glass spheres. PQ Corporation operates worldwide more than 60 plants in about 20 countries and has one of the most comprehensive global manufacturing and distribution networks serving a large variety of industries with a broad range of environment friendly products.

Doucil® MAP zeolites

Doucil MAP zeolites are synthetic crystalline aluminosilicates of the second generation for application in Detergents with the following formula:

$$\text{Na}_2\text{O} \cdot x\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot y\text{H}_2\text{O}$$

A and P type zeolites have the same chemical formula, but are very different in crystal structure, which lends them very different properties. Phosphate-free products based on zeolite 4A were introduced in 1983 and in combination with a polycarboxylate co-builder 4A has since been the builder system for many detergent powders in US, EU and Asia.

In 1994 Doucil A24 was introduced, a P-type zeolite specifically designed to function as a more efficient detergent builder. Doucil A28 was introduced as a variant a few years later to meet specific customer requirements.

Through particle engineering, PQ are able to control particle size, morphology, porosity and molecular framework to help customers apply zeolites most efficiently in their products and processes.

Control over
- Ca-binding properties
- Granulation behavior and liquid carrying capacity
- Bleach stability

enables to make high performance, environmentally friendly detergents, particularly suitable for low temperature washing.

When dry blended at lower levels zeolites function as flow aid and anti-caking agents. Due to the higher liquid carrying capacity (LCC), the MAP zeolites are much more weight-effective than 4A.

**DOUCIL® Zeolite product range.**

<table>
<thead>
<tr>
<th>DOUCIL®</th>
<th>Doucil A24</th>
<th>Doucil A28</th>
<th>Doucil 4A</th>
</tr>
</thead>
<tbody>
<tr>
<td>TYPE</td>
<td>MAP</td>
<td>MAP</td>
<td>A</td>
</tr>
<tr>
<td>D50 (µm)</td>
<td>1.2</td>
<td>1.7</td>
<td>3</td>
</tr>
<tr>
<td>Loss on ignition (%)</td>
<td>10</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>CEBC (mg CaO/g)*</td>
<td>160</td>
<td>168</td>
<td>148</td>
</tr>
<tr>
<td>Ca-uptake rate (sec)</td>
<td>15</td>
<td>6</td>
<td>30</td>
</tr>
<tr>
<td>LCC (g MI/100 g)</td>
<td>58</td>
<td>62</td>
<td>38</td>
</tr>
</tbody>
</table>

*Effective Calcium Binding Capacity per g. Zeolite on dry basis in the presence of NaCl (0.01 mol/l)*
Structure of Doucil® MAP Zeolites:

Doucil® MAP Zeolites
High quality compounds for high performance Detergents
There are more than 150 types of zeolites (natural and synthetic), which differ chemically as well as physically. Until 1988 the only zeolite suitable for use as a detergent builder was a zeolite of the A type i.e. zeolite 4A in its sodium form. Both P and A-type zeolites in the sodium form have the same general chemical formula:

$$\text{Na}_{2}\text{O} \cdot x\text{SiO}_{2} \cdot \text{Al}_{2}\text{O}_{3} \cdot y\text{H}_{2}\text{O}$$

According to the Löwenstein rule, the lowest value attainable for $x$ (ratio SiO2/Al2O3) in zeolites is 2.0, representing the maximum content of aluminium and consequently also of sodium (the ratio: Al/Na always being approximately 1.0). Sodium is not bound within the crystal lattice, but is present as ions in the zeolite pores. These sodium ions are mobile and can be exchanged by calcium, when the pores are accessible and filled with water. When $x = 2.0$ (maximum aluminium and sodium), the theoretical calcium exchange capacity is at its highest and this is important for detergents, since it allows maximum water softening. Maximum aluminium zeolite 4A ($x = 2.0$) can be produced with an average particle size of 2 - 5 micrometer, which is suitable for detergents powders, explaining the early preference for this material in detergents. It was also the material of choice from the perspective of cost and ease of manufacture. P-type zeolites were previously known with higher values for $x$, but these were unsuitable for detergents.

However PQ Corporation has developed a P-type zeolite with a value for $x$ of 2.0 (MAP = Maximum Aluminium P) and an average particle size smaller than for 4A zeolites at around 1.0 micrometer, which is ideal for detergent applications (figure 1). In this new form of P-type zeolite, the accessibility of the sodium is excellent. This product is known as DOUCIL A24 and is the first zeolite material specifically designed to function as a detergent builder.

Although chemically identical to zeolite 4A, DOUCIL A24 has a completely different physical (crystal) structure and hence its properties are not the same:

**Zeolite 4A**
- rigid single crystals
- particle /crystal size: 1 - 10 µm
- pores of 1 µm
- 19 - 21 % (mobile) water

**Doucil A24**
- flexible layered crystal structure
- particle size: 0.7 - 2 µm
- agglomerates of smaller crystallites
- pores of 0.3 µm
- 6 - 12 % (immobile) water

**A28**
- flexible layered crystal structure
- particle size: 2.2 - 3.5 µm
- agglomerates of smaller crystallites
- pores of 0.3 µm
- 18 - 22 % (immobile) water

**Comparison of structures of zeolites 4A and DOUCIL A24**

![Fig. 1 Particle sizes of Doucil A24 and 4A](image)
Calcium Binding Properties

Calcium Uptake Rate (Kinetics)
Owing to its very small crystal size, DOUCIL MAP have a very high surface area when compared to zeolite 4A (40m²/g versus 1m²/g, by N₂ adsorption). The open intercrystalline network system of DOUCIL MAP allows rapid diffusion in and from the crystallite surfaces. These structural differences give DOUCIL MAP much better accessibility and this results in a much higher Calcium Uptake Rate than with zeolite 4A, which is especially significant at lower temperatures (figure 2).

Calcium Effective Binding Capacity
As DOUCIL MAP and zeolite 4A have the same maximum exchangeable sodium content, theoretically they should have the same maximum exchange capacity for calcium. However, builder capacity is limited by the equilibrium between the amount of calcium and sodium in the builder and the concentrations of these ions in the wash liquor. This equilibrium depends on the binding strength of these ions in the builder (selectivity).

Stronger binding of calcium by DOUCIL MAP leads to a higher effective exchange and lower calcium concentrations in the liquor. The smaller pore size allows more extensive Ca-framework interactions and the flexible nature of the P-type framework gives easy distortion to maximize the Ca-framework interaction energy. As a consequence, DOUCIL MAP binds calcium ions much more strongly than zeolite 4A (figures 3,4).

In order to simulate practical washing conditions a new test was developed known as Calcium Effective Binding Capacity. In this test the calcium binding capacity is measured in the presence of sodium ions. The sodium ion concentration chosen is representative of standard European washing conditions.

Due to its higher selectivity, especially at higher calcium loadings, and its faster kinetics, Doucil MAP is 10 - 30% more weight effective than zeolite 4A as a water softener under practical washing conditions (figure 5).

As a consequence of the superior calcium binding kinetics of DOUCIL A24 and the lower calcium concentrations reached in the wash, there is less need for a co-builder. It is therefore possible to minimize the use of expensive co-builders, such as polycarboxylates (co-polymers of acrylic acid and maleic anhydride) or even eliminate them completely.

Water softening performance of DOUCIL A24/28 compared to zeolite 4A
- 10 - 30% more efficient in calcium binding
- Superior low temperature performance
- More effective under severe washing conditions
- Feasibility of omitting/reducing expensive co-builder (polycarboxylates)
Bleach stability

Environmental concerns regarding boron and the advent of non-tower processing technology have caused the industry to look again at percarbonate bleach.

In detergent powders, decomposition of bleach (such as percarbonate) is dominated by a mechanism involving the transport of mobile species across surfaces. Percarbonate decomposition is caused by exchange of water and peroxide, Na\textsubscript{2}CO\textsubscript{3}...1.5H\textsubscript{2}O\textsubscript{2}+H\textsubscript{2}O–Na\textsubscript{2}CO\textsubscript{3}...H\textsubscript{2}O+1.5H\textsubscript{2}O\textsubscript{2} followed by decomposition of peroxide, accelerated by e.g. alkali and transition metals.

The presence of mobile water therefore reduces bleach stability. Moisture can be present from other ingredients in the detergent base, or due to permeability of the detergent pack. Moisture presence also limits storage stability of other sensitive ingredients such as enzymes and perfumes. Proton NMR studies show water associated with DOUCIL A24 to be more tightly bound than that of 4A. Low mobility will inhibit transport and therefore improve bleach stability.

From the water adsorption isotherms of DOUCIL A24 and 4A (figures 6, 7) it can be seen that DOUCIL A24 rehydrates slowly.

Water uptake for zeolite 4A is extremely fast and as a result, it is practically impossible to keep this zeolite at a solids content above 80%. By contrast, water uptake for DOUCIL A24 is slow, allowing storage at lower water content. This zeolite is normally supplied at approximately 90% dry solids content. As a consequence, storage stability of detergent powders containing percarbonate is far superior for DOUCIL A24 than for zeolite 4A (figure 8).

Bleach stability

- Desiccant properties
- Improved bleach stability
- Allows use of percarbonate based bleaching systems
- Less/no carbonate required

A28 is supplied at about 80%DS. As the moisture is less mobile than in 4A, this still creates a superiority over 4A. However, due to the higher total moisture, A28 does not provide the ‘water sink’ function as A24. Effect on bleach stability will be lower than A24, but still superior to 4A.

Liquid carrying capacity

Detergent powders contain solid and liquid components, e.g. surfactants. In order to maintain a free flowing detergent powder, the solid components have to "carry", or absorb the liquids. Detergent formulators are often forced to use excessive amounts of solid builders (phosphate and/or zeolite) or even add other solids (as fillers), simply to be able to include sufficient liquid actives in their formulations.

Standard tests for assessing the Liquid Carrying Capacity of solid materials show that DOUCIL A24 has far superior liquid carrying characteristics, exceeding even zeolite 4A by approx. 50% (figure 7). Liquid carrying capacity of phosphates and soda is extremely poor.

The very high liquid carrying capacity of DOUCIL zeolites makes possible the production of detergent powders by non-tower processing routes, thus saving on capital investment and
energy costs. It offers formulators the freedom to further optimize their formulations, minimizing zeolite use and reducing or omitting fillers.

The small pore size of DOUCIL A24 provides better capillary action and strengthens liquid retention. Hence A24 is less prone to surfactant bleeding than zeolite 4A. As a consequence detergent products containing high surfactant levels and DOUCIL A24 have superior flow properties.

**Liquid Carrying Capacity**

- 50% increase in liquid carrying capacity A24 over zeolite 4A
- material of choice for ultra compact formulations
- preferred material for non-tower processing routes
- Less bleeding of surfactants
- Less/no fillers required

**Compatibility with silicate in spray tower processes.**

The introduction of zeolite 4A in spray dried powders may create a problem, as it is not fully compatible with silicate in this drying process. The silicate can act as an adhesive, forming unacceptable levels of larger agglomerated zeolite 4A particles during drying (so called ‘insolubles’). As a result formulators are recommended to either partly postdose silicate in solid form or reduce silicate levels dramatically.

Zeolite Doucil A24 /A28, due to the physical particle shape, is more compatible with silicate in the spray-drying process.

Therefore, introducing Doucil A24 or A28 facilitates the further use of silicate, thus preserving its beneficial properties e.g. in areas of powder structuring, corrosion protection, improving bleach stability in the wash, building and anti-redeposition.

For slurry application A28 is recommended as more cost-efficient whereas A24 is to be preferred for dry applications where the lower moisture level is more relevant and provides benefits.

The consistent quality of PQ zeolites avoids frequent re-adjustments of process parameters, which is experienced as an important benefit by detergents manufacturers.

**Granulation processes**

Zeolite 4A, A24 and A28 can all be used in granulation processes, but the benefit of each quality depends on the application.

4A is useful when low levels of surfactants are to be incorporated. A24 ,due to its much higher absorption capacity and low moisture level, is ideally suited for copact powders where high levels of surfactants are to be loaded onto relatively low levels of carrying materials and where storage stability is critical.

A28 has similar or higher absorption capacity as A24, but at a slightly higher particle size and has been shown to be particularly advantageous in granulation processes where high surfactant levels are to be added at high speed.

**Flow Aid**

**Anti-caking**

When dry-blended at lower zeolite levels, Doucil zeolites through their high liquid absorption capacity, can act as a flow aid and anti-caking agent in powder formulations. Actual zeolite levels are the formulator’s choice but recommended levels are generally in the range 2-4 %.

**Doucil MAP Zeolites**

**Conclusions / key features**

- Robust builder performance under a wide range of conditions, including low temperature washing.
- High liquid absorption capacity for Doucil A24/28. Allowing more concentrated products to be formulated.
- Doucil zeolites exhibit very consistent product quality enabling customers to minimize process adjustments.
- High product (bleach) stability and ease of processing.
- Safe for human and environment.
- free of legislative restrictions.
- Wide acceptance by detergent manufacturers and consumers.
Packaging

Doucil zeolites are available in bulk, big bags or small bags, fitted with a PE inner layer.

Storage and handling.

Doucil zeolites are not particularly hygroscopic, but to preserve their properties it is recommended that they are stored in dry conditions.

Zeolites: Safe for human and environment

It has long been known that detergents can have a considerable impact on the environment. In the 1970’s issues regarding eutrophication of surface water, with excessive formation of algae and subsequent oxygen deficiency led to a search for detergent phosphate substitutes. In the 1980’s zeolite found worldwide acceptance as an environmentally friendly builder for use in “zero P” formulations and has replaced sodiumtripolyphosphate (STPP) in many countries in Europe, America and Asia. With the ongoing concern for water quality this trend still continues.

Tests by independent consumer organizations have demonstrated excellent performance for the zeolite based formulations compared with the phosphate containing products.

The introduction of zeolites in detergents allowed detergent formulators to make more concentrated formulations. Introduction of these so-called “compact” and “supercompact” products, in combination with new dosage instructions to consumers, has significantly reduced the load of detergent chemicals on the environment.

Detergent zeolites have undergone extensive toxicological studies and have been shown to be nontoxic in living organisms.

Health and Safety

Material Safety Data Sheets providing detailed toxicological and handling information on PQ Corporation zeolites for detergent applications are available upon request.