The core business of CP Kelco is hydrocolloids. CP Kelco holds #1 positions in pectin, xanthan gum, and CMC (sodium carboxymethylcellulose - a versatile, water soluble, cellulose-based polymer), as well as a leading position in carrageenan.

CP Kelco has been producing CMC since the early 1940’s and has extensive knowledge of the manufacturing process and the products. Backed by its customers’ cooperation and support, the company has grown into the world’s leading producer of CMC.

CP Kelco manufactures CMC at three production sites: in Finland, Sweden, and in the Netherlands. The quality of our product meets the requirements of both new and longstanding customers.

Manufacturing sites in Europe

Åänekoski

Nijmegen
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CMC stands for carboxymethylcellulose. However, CMC is more correctly the sodium salt of carboxymethylcellulose. It is derived from cellulose, which is made water-soluble by a chemical reaction. The water-solubility is achieved by introducing carboxymethyl groups along the cellulose chain, which makes hydration of the molecule possible.

The substituents are irreversibly linked to the cellulose backbone with ether bridges, and thus, CMC belongs to the group of substances called cellulose ethers. It is important to note that the carboxymethyl group has an acid function meaning that CMC is an anionic polyelectrolyte.

CMC has many interesting properties when dissolved in aqueous solutions, but this will depend on the CMC grade and the solution conditions.
The cellulose is carefully selected to meet the very strict quality requirements of the end product. It is first treated with sodium hydroxide. Alkali cellulose is formed in the reaction between cellulose and sodium hydroxide. This is a crucial step in the process to ensure that the cellulose is homogeneously converted to alkali cellulose.

CMC is produced from cellulose and monochloroacetic acid (MCA) and with sodium hydroxide (NaOH) as the third essential ingredient. The different steps in the CMC process are described in the flow sheet below.

The alkali treatment step is commonly known as mercerization. The alkali cellulose is accessible and reactive towards monochloroacetic acid, which is added to the reactor either as free acid—MCA, or as its sodium salt—NaMCA.

Structure of cellulose and of sodium carboxymethylcellulose

After completion of the different reaction steps the product contains about 25-35% of by-product salts (sodium chloride and sodium glycolate). It can be dried as it is (technical grade CMC) or neutralized and refined by washing either to minimum 98% purity (FINNFIX® CMC purified grades) or minimum 99.5% purity (CEKOL® cellulose gum grades).

The basic elements of PAC (polyanionic cellulose) are similar to those of CMC. It is, however, made from specially selected cellulose raw material and manufactured under specific process conditions that ensure the unique characteristics typical of PAC.
To serve its diverse markets, CP Kelco water-soluble polymers are produced in a large number of grades with a variety of specifications and performances. The different grades are marketed under different product trademarks:

**CMC for industrial applications. Available as purified and technical grades.**

**Cellulose gum for food, cosmetics, personal care, and pharmaceuticals.**

**Special CMC grades for pharmaceuticals.**

**PAC for oil and gas drilling.**

**Semi-pure PAC for oil and gas drilling.**

**Special CMC grades for use as thickener in textile printing pastes.**

**Efficient binders developed for use in building products.**

**Purified cellulose ether products specially developed for use in water-based emulsion paints.**

**Liquid pumpable CMC dispersion. An attractive alternative to powder CMC, when dissolution capacity is a constraint.**

More detailed information about CP Kelco’s CMC products can be found in the brochure “Standard Grades & Graphs of CMC”.

The CAS number for Sodium CMC is 9004-32-4.
Properties of CMC Solutions

1. Dissolution of CMC

The method of dissolving the CMC and the extent of agitation (shear) during dissolution, will ultimately influence the final viscosity of the solution. The solvent, the chemical composition of the CMC and the shear history of the final solution affect the dissolution properties of CMC, i.e. hydration of the CMC molecules. This means that standardized conditions for CMC dissolution are essential for viscosity control of the resulting solution.

The principle of dissolving CMC is to wet all particles as quickly as possible before the viscosity starts to develop. CMC is by nature hydrophilic (“water-loving”), which means that the CMC particles will instantly start to swell (hydrate) and dissolve when dispersed in water. Therefore, the mixing device used must be efficient enough to keep the entire liquid in motion to avoid agglomeration or lump formation. The mixer should create a strong downstream flow in the center of the dissolution tank and CMC should be added to the vortex formed by the stirrer (Figure 1). It is essential to emphasize that the rate of CMC addition must be slow enough (and even) to permit the particles to become individually wetted.

Addition can be done through a funnel or more preferably with an inductor. However, the rate of addition must be balanced to minimize viscosity build up of the aqueous phase while the CMC is being added.

CMC shows good solubility in both cold and hot water. The rate of dissolution increases at elevated temperatures because the viscosity of the solvent and of the developing CMC solution is lower at high temperature. The dissolution rate of the CMC molecule is independent of temperature. When heating is possible, a suitable (and recommended) temperature to prepare a CMC solution is at about 50-60 °C.

The dissolution rate of CMC also depends on the particle size. Provided that all particles have been individually wetted and no lumping occurs, a fine powder will always dissolve faster compared to a more coarse material. The dissolution profile for different particle sizes is illustrated in Figure 2, expressed as the torsion experienced by the stirrer.

Figure 1: Dissolving of CMC

Figure 2: The dissolution time of several particle size ranges expressed in torque values
Recommended solution concentration for some CMC grades, to achieve a solution viscosity of about 2000 mPa\(\text{s}\) (at room temperature, Brookfield LVT, spindle 3, 30 rpm), is given below.

<table>
<thead>
<tr>
<th>FINNFIX® grade or CEKOL® grade</th>
<th>Max. concentration, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>30</td>
<td>7</td>
</tr>
<tr>
<td>300</td>
<td>3</td>
</tr>
<tr>
<td>4 000</td>
<td>1.5</td>
</tr>
<tr>
<td>30 000</td>
<td>0.8</td>
</tr>
</tbody>
</table>

**Developments in dispersion/dissolution of CMC**

- CMC can be chemically modified, which provides excellent dispersion properties of the powder and retarded dissolution characteristics under neutral or slightly acidic condition. If the dispersion is kept at neutral pH, dissolution will eventually take place, starting after approximately 15-20 minutes. However, by increasing the pH of the dispersion dissolution (at any time) can be triggered (see Figure 3). Even though a chemically modified CMC is an elegant way to control dissolution, this approach has certain limitations and this type of modified CMC can only be used in special applications.

- Specialized dry addition of CMC is employed in certain industries, for instance – in the paper and board coating industries. This simplifies handling of the dry CMC and also eliminates the need of a special dissolution station as well as storage tanks.

- CP Kelco has developed a liquid CMC dispersion specifically for use in the paper coating industry. The dispersion dissolves readily in the coating formulation and is easy to handle. Furthermore, the product has excellent storage stability.

![Hydration profile of special treated CMC, retarded hydration](image)

**Figure 3**: Hydration profile of special treated CMC, retarded hydration.
2. Viscosity and rheology of CMC solutions

The most important and useful property of CMC is its ability to impart viscosity to its aqueous solutions. Solutions can be prepared in a wide range of viscosities. CMC products range from low molecular weight to high molecular weight polymers. The solutions behave, consequently, from almost Newtonian to increasingly pseudoplastic, meaning that the viscosity will change when different physical forces are imposed on it.

The viscosity depends on the shear applied. This is experienced in practice as a decrease in viscosity when a CMC solution is stirred, pumped or sheared in some other way. The pseudoplastic flow behavior is related to de-entanglement and orientation of the CMC molecules in the direction of the flow. A longer molecule (higher molecular weight), as found in **CEKOL 30 000 CMC**, is far more “shear thinning” compared to the shorter chain molecule found in **CEKOL 700 CMC** (see Figure 4). The viscosity of the low molecular weight **CEKOL 30 CMC** is hardly influenced by the shear rate, meaning that the flow behavior of a **CEKOL 30 CMC** solution is almost Newtonian.

**FIGURE 4:** Effect of shear rate on viscosity of a 1% solution of a low, medium, and high viscous **CEKOL** CMC

When the shear stress is increased, the viscosity (resistance to flow) will decrease. The viscosity change is completely and instantaneously reversible and the original viscosity is retained when the shear stops. It is important to note that due to pseudoplastic flow properties of a CMC solution, a measured viscosity value is only valid for a defined shear rate. The term ‘apparent viscosity’ is often used to denote that it is not a definite value but only true under certain conditions.

A property related to the polymeric nature of CMC, and often mixed up with pseudoplasticity, is thixotropy. This has to do with interaction between the long-chain CMC molecules and the development of a three-dimensional structure (network) in the solution. When sufficient shear stress is exerted on a thixotropic solution, the structure can be broken and the apparent viscosity reduced. The viscosity change is reversible but time-dependant and the original viscosity will be retained when the solution remains at rest for a period of time after shearing (Figure 5).

**FIGURE 5:** Thixotropic flow behavior depicted in viscosity profile (Δt illustrative of restore of viscosity)
3. Molecular weight

The viscosity is proportional to the average chain length of the CMC molecule or the degree of polymerization (DP). The average chain length and the degree of substitution determine the molecular weight of the CMC grade. The viscosity increases rapidly with increasing degree of polymerization.

Approximate values for the degree of polymerization and the molecular weight (weight averages) of some CP Kelco CMC grades are given in Table 1.

4. Concentration

The viscosity of a CMC solution increases rapidly with concentration. A fairly good rule of thumb is, that viscosity increases eight to ten fold when the concentration is doubled.

Figure 6 shows the relationship between viscosity and concentration for some purified CP Kelco CMC grades. From this graph it can be seen that a 0.5% solution of a 30 000 grade will show the same viscosity as a 2.5 % solution of a 700 grade. However, this does not imply a similar functionality in applications because the functionality depends on multiple additional factors.

### Table 1: Typical molecular weight averages for some CP Kelco CEKOL CMC and FINNFX CMC grades (DS = 0.8)

<table>
<thead>
<tr>
<th>Grade</th>
<th>Degree of polymerization</th>
<th>Molecular weight, $M_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 000</td>
<td>3 200</td>
<td>750 000</td>
</tr>
<tr>
<td>4 000</td>
<td>2 000</td>
<td>450 000</td>
</tr>
<tr>
<td>700</td>
<td>1 200</td>
<td>270 000</td>
</tr>
<tr>
<td>30</td>
<td>360</td>
<td>80 000</td>
</tr>
</tbody>
</table>

$DS = $ Degree of Substitution

The approximate molecular weight is calculated from:

$$DP \times (162 + 80 \times DS) = M_w$$

![Figure 6: Viscosity of FINNFX / CEKOL CMC of various concentrations in demineralized water](image-url)
5. Temperature

The viscosity of a CMC solution is reversibly temperature dependant i.e. the viscosity decreases when the temperature is increased but the original viscosity is regained when the temperature is lowered to the starting value. Heating for longer periods, in particular if the temperature is above 100 °C may cause loss of viscosity, depending on the grade (see Figure 7). The viscosity/temperature relationship for some purified CP Kelco grades is illustrated in Figure 8.

**FIGURE 7:** Effect of heat treatment on **CEKOL 30 000** CMC 1% in demineralized water

**FIGURE 8:** (left) Effect of temperature on the viscosity of various aqueous solutions of **FINNFIX / CEKOL** CMC (right) Effect of heating at temperatures < 100 °C
6. pH

The viscosity of CMC solutions is stable within a wide pH range (Figure 9). At pH levels of 11-12 and higher, the viscosity is affected due to the high electrolyte concentration prevailing and alkaline degradation (hydrolysis) of the CMC molecule. At a pH <4 the acid form of CMC is beginning to dominate (the Na⁺ counter-ion will be replaced by H⁺). This type of CMC is insoluble in water resulting in a decrease in the viscosity. However, high DS CMC grades and special acid stable grades will show good viscosity stability even under hostile low pH conditions.
The effect of inorganic salts on the viscosity of a CMC solution depends mainly on the ability of the cation of the salt to form a soluble salt with CMC. The compatibility depends, besides the cation, on the concentration of the inorganic salt and the CMC. The properties of the CMC (degree of substitution and the distribution of the substituents) are of paramount importance to enhance the viscosity stability in aqueous electrolyte solutions. It should also be noted that the preparation of the solution often has a strong effect on the final solution viscosity. Generally, the viscosity is less affected if the electrolyte is added to a water solution of CMC rather than dissolving the CMC in the aqueous electrolyte solvent.

Monovalent ions will generally form soluble salts with CMC, while divalent and polyvalent ions form insoluble complexes with CMC. Although calcium CMC is water insoluble, a low number of calcium ions in the sodium CMC molecule will not make it water insoluble. Silver is atypical as well – it forms an insoluble salt despite being monovalent.

For a low substituted CMC grade, considerable differences in viscosity may be seen if salt is added before or after the CMC is dissolved. When salt is added to a CMC solution, it will hardly affect the viscosity (not even after a long storage time) while a CMC dissolved in an aqueous electrolyte solvent may show a much lower viscosity than expected. High substituted CMC is less sensitive towards electrolytes than medium or low substituted grades. The reason for this is that, although some of the sodium ions of the CMC will be replaced, there is still enough unperturbed Na-CMC to maintain the viscosity.

**FIGURE 10:** Effect of electrolyte on solutions of low and medium viscosity CMC
Electrolyte effects are most pronounced on high viscosity grades. For low viscosity grades no effect or even an opposite effect (viscosity increase) may occur. The effect of salt on the viscosity of a CMC solution is illustrated in Figure 10. It should be noted that Figure 10 shows the viscosity behavior when CMC has been dissolved in the aqueous salt solution.

The CMC molecule will change its configuration (coiling will occur) in solution when exposed to various types of electrolytes (salts, acids, or alkalis) often resulting in a decrease in the viscosity. This effect is commonly known as the "polyelectrolyte effect" and is most pronounced in dilute solutions (< 0.5% solute concentration). At higher concentration the effect diminishes because the migration of the counter-ions is restricted due to the high local viscosity in the solution. The presence of an electrolyte will (in most cases) also affect the solubility of the CMC molecule as discussed above. A high viscosity grade is normally more affected by the presence of electrolytes compared to a medium or low viscosity grade since the high viscosity grades are generally used at a lower concentration and this means that the "polyelectrolyte effect" will be more visible. The electrolyte compatibility can be improved by increasing the degree of substitution of the CMC (see § 8). Equally important is the selection of raw materials and process conditions during manufacture. Figure 11 and Figure 12 illustrate some properties of high viscosity grades compared to a medium viscosity grade when the CMC has been dissolved in 5% acetic acid (pH of the solution was 3.4). The CEKOL A grades are specially developed to be highly compatible with various types of acids. Even more important is that solutions of these grades stay transparent while a solution of a standard grade becomes hazy under acidic conditions (see Figure 12).

![Figure 11: Comparison of viscosity of various CEKOL CMC grades in water and in 5% acetic acid](image1)

![Figure 12: Comparison of the clarity of solutions of CEKOL A CMC grades and CEKOL CMC standard products in 5% acetic acid](image2)
The degree of substitution, DS, is one of the most important properties of CMC. It not only influences the solubility of the CMC molecule but also affects the solution characteristics. By definition, the DS is the average number of carboxymethyl groups per anhydroglucose unit. Theoretically, the maximum DS is 3. The normal DS range for commercially available CMC is approx. 0.5 - 1.5. Higher degrees of substitution will normally improve the solubility of the CMC and enhance the viscosity stability in the presence of salts or at low pH.

The degree of substitution of the CMC molecule has a major influence on the solution characteristics. The main effects are summarized in Figure 13.

**FIGURE 13:** Influence of the degree of substitution
Not only the DS level but also the distribution of the substituents along the chain will influence the solution characteristics of the CMC. The rheological behavior of a CMC solution and the compatibility with other soluble components will be affected by the substitution characteristics. An aqueous solution of an unevenly substituted CMC (normally at a DS < 0.7) will often exhibit thixotropic (see Figure 14) behavior due to the development of a three-dimensional network in the solution. This behavior will be more pronounced in mixed solvents. This is illustrated in Figure 15. Both CMC types show a “viscosity bonus effect” (synergy) in this solvent. However, the synergistic effect will be strongly influenced by the distribution of the substituents. This is clearly illustrated by the performance of CMC type I. This type (i.e. CP Kelco CEKOL® 500T cellulose gum) is an efficient gelling agent with a unique distribution of the substituents. Higher degrees of substitution give products having improved resistance to enzymatic degradation. However, these CMC grades are still biodegradable.

![Figure 14: Effect of the substitution pattern on the rheology](image)

![Figure 15: Effect of mixed solvent (glycerin/water) on the viscosity of CMC with different substitution patterns](image)

<table>
<thead>
<tr>
<th>GRADE</th>
<th>visc. (mPa*s), 2% aqueous solution</th>
<th>DS</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>450</td>
<td>0.70</td>
</tr>
<tr>
<td>II</td>
<td>455</td>
<td>0.70</td>
</tr>
</tbody>
</table>
9. Stability

Although CMC has good stability towards degradation – enzymes and oxidants may still degrade it. Enzymes, either added as such or produced by microorganisms, may degrade the cellulose chain, and thus, cause serious, irreversible viscosity decreases.

The normal route of enzyme contamination is via microorganisms, present in the environment. These infect the system where CMC is used and start producing enzymes. An efficient way to stop enzymatic attacks is thus to prevent growth of microorganisms. This can be done by heat treatment or by adding preservative. Heating for about 30 minutes at 80 °C, or about 1 minute at 100 °C is normally sufficient to destroy the microorganisms. Complete inactivation of possibly present cellulolytic enzymes may require a somewhat higher temperature and/or longer time. Some preservatives suitable for CMC solutions are listed below.

Further information about type and amount of preservative should be requested from the preservative manufacturer.

<table>
<thead>
<tr>
<th>Formaldehyde</th>
<th>Phenol</th>
<th>Thymol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dowicide (Dow)</td>
<td>Santobrite (Monsanto)</td>
<td>2-Biphenylol</td>
</tr>
</tbody>
</table>

Suitable preservatives for food, cosmetic and pharmaceutical uses are given below.

<table>
<thead>
<tr>
<th>Sodium benzoate</th>
<th>Sorbates (Na and K salts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium propionate</td>
<td>Methyl parahydroxybenzoate</td>
</tr>
</tbody>
</table>

Oxidants, e.g. chlorine and hydrogen peroxide, cause degradation of the cellulose chain. Oxidative degradation occurs under alkaline conditions in the presence of oxygen. Metal ions, like Fe2+ accelerate alkaline degradation.

To prevent oxidative degradation, CMC solutions should not be exposed to the open air for longer than necessary, especially at elevated temperatures and pH. During prolonged storage, the CMC solutions should be preserved as soon as possible after preparation and (if possible) maintained at neutral pH. Oxygen and sunlight should be excluded.

10. Shelf life

All CMC grades are derived either from wood pulp or, sometimes, also from cotton linter. They are biodegradable and this also means that the shelf life of these products is limited. Consequently, it is important to store these products in a correct way to prevent unnecessary degradation.

Never store CMC in open bags.

CMC is hygroscopic, meaning that it easily absorbs moisture from the environment. The product should be stored in its original packaging, in a dry and well-conditioned place. It is important to keep the storage area dry, clean, and dust free.

The properties of CMC mostly affected during storage are moisture and viscosity.

Provided the product is stored as outlined above, most CMC grades remain in good condition for a period of about 3 years. However, in general it is recommended not to store CMC longer than 1 year, since even during appropriate storage some minor changes in the chemical properties of the product are unavoidable. This is, in particular, the case for high viscosity grades, where as an extra precaution before use, a re-check of the chemical properties already after 6 months storage is recommended.

It is important to use clean equipment when handling CMC, to avoid possible microbial contamination.
In order to achieve a specific viscosity it is possible to blend two or more CMC grades with different viscosities. The resulting viscosity of the blend can be calculated by using the formula:

\[
\log v_b = \frac{a_1 \log v_1 + a_2 \log v_2 + \ldots}{a_1 + a_2 + \ldots}
\]

*Where:*
- \( v_b \) = viscosity of the blend
- \( a_1 \) = the amount of component 1
- \( v_1 \) = the viscosity of component 1
- \( a_2 \) = the amount of component 2
- \( v_2 \) = the viscosity of component 2

If only two components are used the viscosity of the blend can easily be determined from the logarithmic diagram shown in Figure 16.
CMC has been extensively evaluated by both WHO/FAO Joint Expert Committee on Food Additives (Jecfa) and by the Scientific Committee for Food in the European Union. The results of both toxicological evaluations were that no adverse toxicological effects could be identified.

Aquatic organisms are exposed to CMC due to occasional direct discharge of CMC into surface water. No harmful effects to aquatic organisms of various CMC and their intermediates have been detected.

Partial biodegradation of CMC in activated sludge plants also necessitates assessment of the aquatic toxicity of the intermediates formed during the biodegradation process. Tests made with intermediates of CMC (DS=0.7) reveal that the biological treated CMC does not exhibit toxicity. Acute and chronic toxicity of CMC (DS=0.7) and of the biodegradation intermediate of this CMC to aquatic organisms are summarized below. All no-effect concentrations (NOEC) values were the highest concentrations tested.

<table>
<thead>
<tr>
<th>TEST ORGANISM</th>
<th>OECD Guideline</th>
<th>Duration (hours)</th>
<th>Endpoint</th>
<th>CMC concentration, g/l</th>
<th>Intermediate concentration, g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudomonas putida</td>
<td>96</td>
<td>NOEC</td>
<td>1.0</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Selenastrum capricornutum</td>
<td>201</td>
<td>96</td>
<td>NOEC</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Daphnia magna</td>
<td>202</td>
<td>48</td>
<td>NOEC</td>
<td>5.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Brachydanio rerio</td>
<td>203</td>
<td>96</td>
<td>NOEC</td>
<td>2.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* Not determined

The data in the Table is obtained from the publication: Ginkel C.G. van and Gayton S., *Environmental Toxicology Chemistry* 15, 270-274, 1996

Biodegradation of a wide range of CMC types has been studied in laboratory scale with the purpose to simulate conditions on wastewater treatment plants and natural ecosystems. A prolonged Closed Bottle test method was used. The test results show that the rate of biodegradation of CMC is dependent on the molecular weight (see Figure 17). The DS and the rate of biodegradation have an inverse relationship (see Figure 18). This is in line with other tests where CMC solutions have been inoculated with Cellulase. The rate of enzymatic degradation decreases with increasing DS. The biodegradation of all CMC types was >60%, indicating complete biodegradation. Furthermore, CMC (DS=0.6) labelled with 14C in the carboxymethyl group, was subjected to naturally occurring microorganisms in a batch culture. 84% of the 14C was recovered as carbon dioxide after 16 weeks, demonstrating the susceptibility of the carboxymethyl groups to biodegradation.

**FIGURE 17:** Effect of the molecular weight on the rate of biodegradation

**FIGURE 18:** Effect of the degree of substitution on the rate of biodegradation
Compatibility with Other Polymers

1. Nonionic cellulose derivatives

CP Kelco CMC products are compatible with most nonionic cellulose derivatives over a wide range of concentrations. However, when working with blends of CMC and nonionics it is sometimes advisable to select reasonably similar viscosity grades unless very special properties of the blend are requested. Blends of CMC and a nonionic cellulose derivative will, in most cases, show a synergistic effect on viscosity. The polymer blend shows solution viscosities considerably higher than would be expected. This is illustrated in Figure 19, where the viscosity behavior of blends between FINNFIX® 2 000 + EHEC (ethyl-hydroxy-ethyl cellulose) [Figure 19A] and FINNFIX® 300 + MC (methyl cellulose) [Figure 19B] is depicted.

![Figure 19: Examples of viscosity behavior of blends of CMC and other cellulose ethers](image)

2. Other polysaccharides

CP Kelco CMC products are fully compatible with most other polysaccharides. With some, a synergistic viscosity effect may be experienced and with others – the viscosity follows the theoretically expected behavior. A few examples of blends of CMC with different polysaccharides are given in Figure 20.

![Figure 20: Examples of the viscosity effect of blends of CMC and some other polysaccharides](image)
3. Proteins

Proteins are polymers of amino acids and occur in a large number of different shapes. These have several properties in common, one of which is their pH-sensitivity. This makes their water solubility restricted to rather narrow pH-intervals. However, due to the ionic nature of CMC, it can interact with many proteins to form soluble and stable complexes. This is especially important for proteins showing an iso-electric point (the pH where the solubility normally is poorest) near or below neutral. An important example is stabilization of milk protein (casein) with CMC in sour milk products. The iso-electric point of casein in milk is approx 4.6. The reaction of a protein and CMC around the iso-electric point is illustrated below.

**Figure 21:** Formation of a cellulose gum-protein complex

**Figure 22:** Stabilization of casein with CMC
Sodium carboxymethylcellulose, CMC, is one of the most diversified commercial thickening agents with respect to its industrial applications.

A review of some important applications of CMC is compiled below.

### Film formation agent
- Gives a mechanical- and chemical-resistant film

### Binding agent
- Is able to bind large amounts of water

### Stabilising agent
- Keeps suspended particles or dissolved molecules stable through chemical interaction

### Water retention agent
- Prevents water from escaping

### Protective colloid
- Keeps suspended particles stable in suspension

### Thickening agent
- Gives viscosity to an aqueous formulation

<table>
<thead>
<tr>
<th>Field</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food</td>
<td>CEKOL® CMC and NYMCEL® CMC grades, purity criteria min. 99.5%</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>Mainly purified FINNFIX® CMC grades, 98%</td>
</tr>
<tr>
<td>Personal care products</td>
<td>CELFLOW® cellulose ether and purified FINNFIX CMC grades</td>
</tr>
<tr>
<td>Paper coating</td>
<td>CELLUFIX® CMC and purified FINNFIX CMC grades</td>
</tr>
<tr>
<td>Paper sizing</td>
<td>Purified and technical FINNFIX CMC grades</td>
</tr>
<tr>
<td>Ceramics</td>
<td>CELLCOSAN® CMC</td>
</tr>
<tr>
<td>Textile sizing</td>
<td>Technical FINNFIX CMC grades</td>
</tr>
<tr>
<td>Paints</td>
<td>CELPOL® PAC grades and also technical FINNFIX CMC grades</td>
</tr>
<tr>
<td>Adhesives</td>
<td>Purified and technical FINNFIX CMC grades</td>
</tr>
<tr>
<td>Mineral flotation</td>
<td>Purified and technical FINNFIX CMC grades</td>
</tr>
<tr>
<td>Textile printing</td>
<td>Purified and technical FINNFIX CMC grades</td>
</tr>
<tr>
<td>Detergents</td>
<td>Purified and technical FINNFIX CMC grades</td>
</tr>
<tr>
<td>Drilling fluids</td>
<td>Purified and technical FINNFIX CMC grades</td>
</tr>
</tbody>
</table>
MODIFICATIONS OF CMC

There are a number of interesting possibilities to modify the CMC molecule either by using CMC as raw material to add other functional groups or modifying CMC through chemical or physical treatments. A few examples will briefly be reviewed in this paragraph.

• ASSOCIATIVE PERFORMANCE
Associative performance can be achieved through a hydrophobic modification of the CMC molecule. An example of such a modification is given below, where CMC is reacted with Alkyl Ketene Dimer (AKD), giving a surface active hydrophobic CMC molecule (J.M. Huber patent).

Depending on the degree of hydrophobicity as well as the chemical composition of R1 and R2 respectively, unique and specific functionality can be achieved with this modified CMC.

\[
\begin{align*}
\text{R}_1 - \text{CH} &= \text{C} - \text{CH} - \text{R}_2 + \text{CMC} \\
\text{O} &\quad \text{C}_6 - \text{C}_22
\end{align*}
\]

\[
\begin{align*}
\text{O} &\quad \text{R}_2 \\
\text{R}_1 - \text{CH}_2 - \text{C} - \text{C} - \text{O} - \text{CMC} \\
\text{H}
\end{align*}
\]

• CROSSLINKING
Crosslinking of CMC can be done either through a chemical reaction or through heat treatment. The degree of crosslinking will affect the water solubility of the CMC molecule and, at a certain point, the molecule becomes insoluble in water. However, this molecule is still very hydrophilic and has the ability to absorb and retain considerable amounts of water or aqueous media. This ability combined with the fact that such a CMC type is still inherently biodegradable, makes it attractive for use as a superabsorbent.

Special types of crosslinked CMC, so called cross-carmellose sodium, are extensively used in the pharmaceutical industry as disintegrants for tablets.

Low or moderate crosslinking of the CMC molecule creates a three-dimensional structure in solution, which affects the rheological properties. This type of CMC shows thixotropic flow behavior (see Figure 5) making it attractive for use as an adhesive or as a thickener in applications, where workability and flow characteristics of the products are key elements.

ANALYTICAL METHODS FOR CMC

Analysis may be carried out by various methods. CP Kelco CMC products are analyzed according to the following standard methods.

1. Moisture content
Weigh accurately 5 g sample of CMC in a beaker.
Let it dry for 4 hours at 105 ± 3 °C.
Cool the beaker in a desiccator for 30 minutes and weigh it again.

\[
\text{Moisture \%} = \frac{(A - B) \times 100}{A}
\]

Where: \( A \) = weight of the original sample, g
\( B \) = weight of the dried sample, g
2. Viscosity

Depending on the grade of CMC, the viscosity is determined in 4%, 2% or 1% aqueous solutions. Mix the sample slowly into distilled water by stirring with a wire mixer at 550-600 rpm. Increase the speed of the mixer to 700 ± 100 rpm and stir until the sample is completely dissolved. Stabilize the temperature of the solution in a water bath to 25 ± 0.5 °C. Viscosity is measured with a Brookfield LVT viscometer using a spindle and speed according to the table below.

<table>
<thead>
<tr>
<th>Viscosity range in mPa·s</th>
<th>Spindle</th>
<th>Speed, rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 100</td>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>100 - 500</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>500 - 2 000</td>
<td>3</td>
<td>60</td>
</tr>
<tr>
<td>2 000 - 4 000</td>
<td>3</td>
<td>30</td>
</tr>
<tr>
<td>4 000 - 20 000</td>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>&gt; 20 000</td>
<td>4</td>
<td>12</td>
</tr>
</tbody>
</table>

3. CMC content of technical grades

Determine the moisture content of CMC.

Wash 1 - 1.5 g CMC free from salts with 80% ethanol.

Dry and weigh the residual CMC.

\[
\text{CMC content, } \% = \frac{A \times 10000}{(B \times (100 - C))}
\]

Where: 
- \(A\) = weight of the dried residue, g
- \(B\) = weight of the sample, g
- \(C\) = moisture of the sample, %

4. CMC content of purified grades

Determine the sodium chloride and sodium glycolate contents of CMC according to the instructions of ASTM D 1439.

\[
\text{CMC content, } \% = 100 - A - B
\]

Where: 
- \(A\) = sodium chloride content, %
- \(B\) = sodium glycolate content, %

5. Degree of substitution, DS

Weigh accurately 0.5 g sample of pure 100% CMC (salt free) in a crucible.

Ignite the sample first over a small flame until the sample becomes charred, followed by 45 minutes in a kiln at 650 °C. Ash should be grayish white.

Dissolve the ash in a small amount of distilled water and titrate with 0.1 N sulphuric acid and use methyl red as an indicator.

\[
DS = \frac{(0.162 \times B)}{(1 - 0.080 \times B)}
\]

Where: 
- \(B\) = consumption of 0.1 N H2 SO4, ml
- \(G\) = weight of 100% CMC, g

6. Determination of pH

Dissolve CMC in distilled water into 1% solution and measure pH.
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