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Application of Cellulose Derivatives in Mineral Processing

Ashok Kumar, Kaman Singh and Satya Prakash Gupta

Abstract

Cellulose derivatives (CDs) have been recognized as an anionic water-soluble, non-toxic, biocompatible and biodegradable polysaccharide. The CDs have been used as a viscosity regulator, thickening agent, sizing agent and coating agent and emulsion stabilizer, electrode binder in various industries. These characteristics properties of CDs are associated with hydroxyl groups/functionalized groups present in their structure. The CDs have significant advantages in various fields including several industrial applications such as mineral processing, palletisation process, oil drilling industrial applications due to their non-toxic and selective properties. Moreover, The CDs have been extensively used as a depressant, dispersant as well as flocculants in mineral processing from various ores. During the mineral processing like flotation of sulfide minerals highly toxic inorganic species were used as dispersant and depressant which ultimately causes environmental toxicity. Therefore, there is a current need to introduce CDs as various alternative nontoxic dispersant and flocculants. This chapter emphasized an overview of the application of CDs in mineral processing including the structure, properties of the commonly used minerals processing.

Keywords: cellulose derivatives (CDs), mineral processing, depressant, dispersant

1. Introduction

Cellulose has been recognized as the most abundant polymer on the planet, making it an important raw material for a variety of applications. Because of its potential use in the development of biofuels, cellulose has recently gained attention. However, cellulose's flexibility has been demonstrated in a variety of applications. It can also be chemically modified to produce cellulose derivatives (CDs) [1]. The two main classes of cellulose derivatives (CDs) were Cellulose ethers and cellulose esters, which have different physicochemical and mechanical properties. The Cellulose derivatives (CDs) have been widely used in a wide range of applications, including particle dispersion, flocculation processes, surface treatment, and so on. Tablet binding, thickening, film-forming, water retention, adhesion, and suspending and emulsifying agents are some of the most common uses of cellulose derivatives in tablet and capsule formulations. Natural aggregates are still important in cement production, though high-purity sources are becoming harder to come by. The CDs have been used to "inert" the aggregate to the cement formulation to prevent clay minerals associated with the aggregates from adversely affecting the

cement formulation by adsorption of plasticizers and resulting property alteration [2]. The CD's application in the upstream petroleum industry, such as exploration, drilling, development, and distribution, has recently sparked renewed interest. Adding CDs to fluids, in particular, can have important benefits for improved oil recovery and well drilling, such as changing fluid properties, rock wettability alternation, advanced drag reduction, sand consolidation strengthening, minimizing interfacial friction, and increasing mobility of capillary-trapped oil [3].

For the depression of copper minerals, inorganic modifiers such as sodium cyanide, sodium sulphide or hydrosulphide, ferrocyanides, and Nokes reagent are frequently used. These reagents were very reliable, but their use has recently raised environmental concerns. CDs depressants have been investigated as possible alternatives to avoid this issue. The use of polysaccharides namely starch, dextrin, and carboxymethylcellulose (CMC) in sulphide minerals have been identified [4–11]. A frother is produced by combining hydroxypropylmethylcellulose (HPMC) or hydroxyethyl methylcellulose (HMC) with at least one non-ionic organic surfactant or polyglycol esters. The new cellulose-based frothers can be used in mineral processing plants to allow for the processing of larger amounts of minerals without requiring major changes to existing equipment. This book chapter describes the structure, properties of the commonly used CDs in minerals processing.

2. Background

Raw material demand has steadily increased on a global scale as a result of demographic and economic developments. If current trends in raw material use intensify, Industrial technologies will be unable to meet this growing demand. As a result, it is necessary to highlight that raw material (CDs present case) production must be supported as a strategic necessity, requiring the development of new technologies that can help meet this upcoming raw material demand. An additional challenge for the mining industry is that, as the world's mineral reserves are exhausted and demand for metallic raw materials rises, it will be designed to process ever greater amounts of low-quality mined material to manufacture concentrates in adequate quantities to meet current and potential demand. As a result of these requirements, minerals trapped in tailings ponds have started to receive interest as a potential source of raw materials, as many existing ore bodies near depletion. As a result, the mineral processing industry was interested in finding new solutions for the treatment of tailings to reprocess. It's worth remembering that the global amount of tailings was enormous, and if an available processing method could be developed, this could translate into a massive feed stream for the metals industry [11]. One of the most commonly used enrichment methods in mineral processing is froth flotation separation. The flotation separation is used in the processing of metals like copper, gold, and platinum to produce concentrates that can be refined economically. Efforts are currently being made to better understand the various phenomenon like frother phenomenon, adsorption etc. and how to regulate it, but no genuinely innovative frother method has been proposed, as most studies are focusing on CDs [12, 13]. As soon as synthetic polymers (CDs) were introduced into mineral processing, combinations with cellulosic materials became available and the importance of CDs came to light.

Selective depressants were essential components of any flotation reagent scheme that aims to separate various minerals selectively. Inorganic depressants have been used often. Many of these depressants, especially those used in differential sulphide flotation, are highly toxic and unsuitable for use in the environment. Sodium cyanide, sodium dichromate, sulfur dioxide, arsenic trioxide, phosphorous

pentasulfide, and other depressants were examples. Since some of these inorganic depressants were reducing agents, they can be oxidized in aerated flotation pulps. The use of a lot of reagents was normally the result. Polysaccharides, on the other hand, were non-toxic and biodegradable natural organic polymers. They're much less expensive and less prone to oxidation than inorganic depressants. These characteristics not only make them perfect flotation reagents, but they have also shown promise as selective depressants in a variety of differential mineral flotation systems. For nearly 70 years, cellulose derivatives (CDs) and polysaccharides/CDs have been used in the mineral industry as depressants for iron oxides, naturally hydrophobic minerals, and rock-forming gangue minerals. They've also been reported to be selective in sulphide mineral differential flotation [14].

3. Cellulose derivatives (CDs)

Cellulose is a linear polymer made up of D-glucose monomers linked together by D- β (1–4) linkages and arranged in repeating cellobiose units, each of which contains two anhydroglucoses (**Figure 1**). Cellulose has a long molecular chain and the three hydroxyl groups have a high hydrogen-bonding ability. The hydrogen atoms of hydroxyl groups in cellulose's anhydroglucose units were replaced with alkyl or substituted alkyl groups to create cellulose ethers, which have a high molecular weight. The molecular weights, chemical structure, and distribution of substituent groups, as well as the degree of substitution and molar substitution, determine the commercially important properties of cellulose ethers (where applicable) [1]. The solubility, viscosity in solution, surface activity, thermoplastic film characteristics, and resilience against biodegradation, heat, hydrolysis, and oxidation were all examples of these properties. The molecular weights of cellulose ether solutions were specifically correlated to their viscosity. Methylcellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), hydroxypropylmethylcellulose (HPMC), carboxymethyl cellulose (CMC), and sodium carboxymethyl cellulose have several identified of the most commonly used sodium-carboxyl methylcellulose (Na-CMC). However, the CDs HPMC, HPC, microcrystalline cellulose (MCC), silicifiedmicrocrystallinecellulose (SMCC), HEC, sodium carboxymethylcellulose (SCMC), ethylcellulose (EC) methylcellulose (MC), oxycellulose (OC), etc. have also been used in allied industries **Table 1** [14, 15].

3.1 Carboxymethylcellulose (CMC)

Carboxymethyl cellulose (CMC) has been introduced as a cellulose derivative in which some of the hydroxyl attached to them ($-\text{CH}_2\text{-COOH}$) make up the cellulose backbone (**Figure 2**). The alkali-catalyzed reaction of cellulose with chloroacetic acid produces it. The polar carboxyl groups in cellulose (organic acid) rendering it soluble and chemically reactive. The degree of substitution of the cellulose structure (i.e., how many of the hydroxyl groups have taken part in the substitution

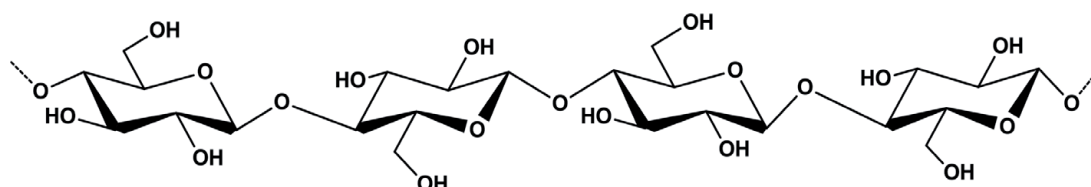


Figure 1.
 Structure of cellulose (repeating unit of glucose) shows the d-glucose units are linked through β -1, 4 bonds.
 ----O represents the continuation of the polymeric chain.

| Cellulose ethers | | |
|------------------|---|-------------------------------------|
| Category | Group R = H or | Derivatives |
| Alkyl | -CH ₃ | Methylcellulose (MC) |
| | -CH ₂ CH ₃ | Ethylcellulose (EC) |
| | -CH ₃ or -CH ₂ CH ₃ | Ethylmethylcellulose (HMC) |
| Hydroxyalkyl | -CH ₂ CH ₂ OH | Hydroxyethylcellulose (HEC) |
| | -CH ₂ CH(OH)CH ₃ | Hydroxypropylcellulose (HPC) |
| | -CH ₃ or -CH ₂ CH ₂ OH | Hydroxyethylmethylcellulose (HEMC) |
| | -CH ₃ or -CH ₂ CH(OH)CH ₃ | Hydroxypropylmethylcellulose (HPMC) |
| | -CH ₂ CH ₃ or -CH ₂ CH ₂ OH | Ethylhydroxyethylcellulose (EHC) |
| Carboxyalkyl | -CH ₂ COOH | Carboxymethylcellulose (CMC) |
| Cellulose ester | | |
| Organic | H or -(C=O)CH ₃ | Celluloseacetate |
| | -(C=O)CH ₃ | Celluloseetriacetate |
| | H or -(C=O)CH ₂ CH ₃ | Cellulosepropionate |
| | H or -(C=O)CH ₃ or -(C=O)CH ₂ CH ₃ | Celluloseacetatepropionate (CAP) |
| | H or -(C=O)CH ₃ or -(C=O)CH ₂ CH ₂ CH ₃ | Celluloseacetatebutyrate (CAB) |
| Inorganic | H or -NO ₂ | Nitrocellulose (cellulose nitrate) |
| | H or -SO ₃ H | Cellulose sulfate |

Table 1.
Some most common class of cellulose derivatives (CDs).

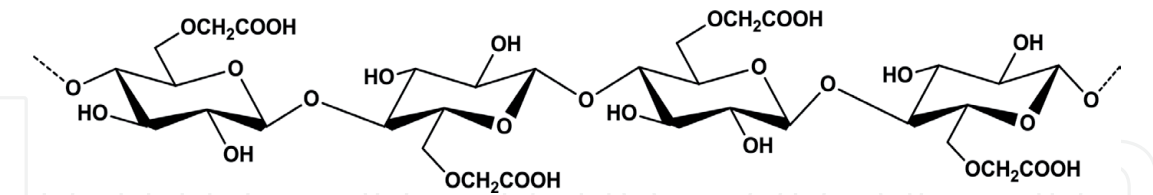


Figure 2.
Structure of Carboxymethylcellulose (repeating unit of glucose) shows the d-glucose units are linked through β-1, 4 bonds. ----O represents the continuation of the polymeric chain.

reaction), as well as the chain length of the cellulose backbone structure and the degree of clustering of the Carboxymethyl substituents, impact the functional properties of CMC.

The CMC was also used in the oil drilling industry as a viscosity modifier and water-retaining agent in drilling mud. CMC has been used to make poly-anionic cellulose (PAC) which was often used in oilfield operation. Some researchers performed surface modification and used surfactant to adjust the surface tension of the carbon fiber to improve dispersion. The wettability of carbon fibers by water was effectively improved by ozone surface treatment, which increases the fiber-matrix bond [15]. The silane treatment of carbon fibers enhances the mechanical properties of carbon fiber reinforced cement, according to Xu and Chung [16]. Wang et al. [17] used hydroxyethyl cellulose and an ultrasonic wave to support fiber dispersion

in carbon fiber-reinforced cement-based composites. As a dispersing agent, CMC was used. CMC can increase carbon fiber dispersion because it has both hydrophobic and hydrophilic sides as a dispersant. Concerning carbon fiber dispersion, the effects of CMC concentration and solution pH were investigated [18].

3.2 Sodiumcarboxymethylcellulose (CMC)

Sodium carboxymethyl cellulose (CMC) is one of the most important products of cellulose ethers, which have been cellulose derivate with an ether structure produced by natural cellulose modification (**Figure 3**). Since the acid form of CMC has a low water solubility, it is generally preserved as sodium carboxymethylcellulose, which is widely used in many industries and is commonly referred to as monosodium glutamate [19, 20].

Na-CMC can be supplied stably and in large quantities, and its technical and cost efficiency was uniform and robust as compared to botanical natural polysaccharides such as tragacanth, arabic, and gua gums, or microbiological polysaccharides such as xanthan gum, which perform the same functions. Na-CMC-Na can thus be recommended as a suitable additive for coal-water slurries (CWS) as an energy supply source with low cost, stability, uniform property, and broad quantity supply capability [21]. A bituminous coal sample from Zonguldak (Thermal Code No. 434) was also used in addition to the brown coals. In all of the samples, Na-CMC was used as a stabilizer in the preparation of CWS [22]. Besides this Na-CMC was used to relieve dry, irritated eyes. Common causes for dry eyes include wind, sun, heating/air conditioning, computer use/reading, and certain medications. Electronics, pesticides, leather, plastics, printing, ceramics, and the daily-use chemical industry are only a few of the fields where Na-CMC has been used.

3.3 Hydroxyethyl cellulose (HEC)

Hydroxyethylcellulose (HEC) (**Figure 4**) has been introduced a polysaccharide derivative with gel thickening, emulsifying, bubble-forming, water-retaining and stabilizing properties. It is a white, yellowish-white or grayish-white, odorless and tasteless, hygroscopic powder [23, 24].

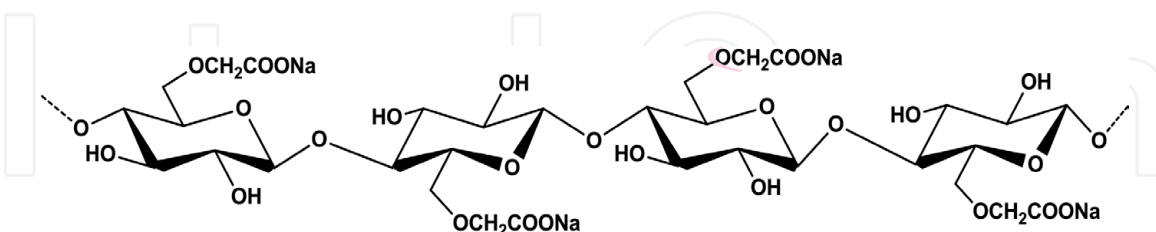


Figure 3. Structure of sodium carboxymethylcellulose (repeating unit of glucose) shows the d-glucose units are linked through β -1, 4 bonds. ----O represents the continuation of the polymeric chain.

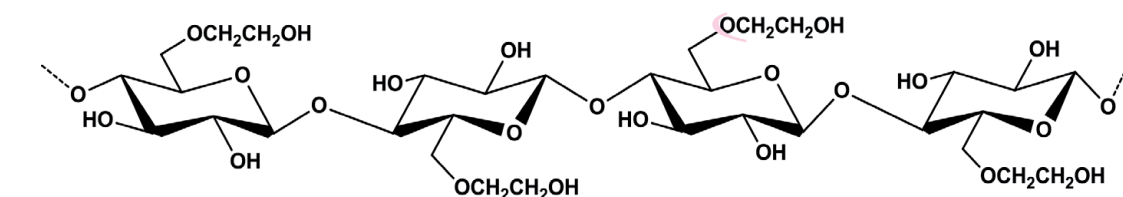


Figure 4. Structure of hydroxyethylcellulose (repeating unit of glucose) shows the d-glucose units are linked through β -1, 4 bonds. ----O represents the continuation of the polymeric chain.

Hydroxyethylcellulose (HEC) and its hydrophobically modified derivatives have been widely used in many industrial areas such as pharmaceuticals, cosmetics, textiles, paint and mineral industries including in oil extraction, coating, medication, food, and polymer polymerization. This was non-toxic and inexpensive. Despite this, only a few reports on HEC as a sulphide depressant have been published. The function of hydroxyethyl cellulose (HEC) in the flotation separation of chalcopyrite and galena has been investigated, and the explanation for this has been explained. In the presence of H₂O₂, a small amount of HEC can depress galena flotation but had only a negligible effect on chalcopyrite flotation. HEC was adsorbed on galena surfaces primarily through chemical reactions with oxidation products formed on the surface, and the addition of H₂O₂ can significantly improve HEC adsorption by producing further oxidation products. As a result, its research would be used as a galena depressant in the flotation separation of chalcopyrite and galena, as well as to propose a method for separating copper/lead sulphide minerals. Furthermore, HEC can be used as the stabilizer of beer foam [25–30].

4. Conclusions

Mining is one of humanity's oldest industries, and it has aided in the advancement of technology that has brought us our modern products. The rising demand for mineral-based technological goods, combined with the increasingly difficult and complex method of obtaining raw materials, necessitates more efficient separation and recycling processes. At the same time, the pressures on mineral processing in terms of sustainability and environmental friendliness are making it more difficult to produce minerals as a scarce resource economically viable. Therefore, Cellulose derivatives (CDs), high-molecular-weight condensation polymers made up of basic monosaccharide sugar units, has been applied in mineral processing. Although there were many different types of polysaccharides including their derivatives in nature, widely have been used in the mineral industry, especially in flotation. The chapter which is presented here is a small contribution to the growing understanding of polymer/CD's applications. We thus feel that this chapter is a valuable contribution to the field of mineral processing and its allied areas with a brief description of CDs. Hence in this chapter, we have summarized the current status of important cellulose derivatives employed in mineral processing.

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