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BIOBASED CHEMICALS FOR MINING INDUSTRY

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ABSTRACT

Biobased chemicals for mining industry

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Bio-based chemicals, green chemistry and bioeconomy are emerging trends both in the mining industry and in society in general. This thesis is a literature review, and the aim of this thesis is to review and evaluate promising biobased chemicals for the mining industry. The main interest is in biobased chemicals on industrial scale. Environmental impact of the mining industry is significant and biobased chemicals may decrease the negative impact. Biobased chemicals are part of green chemistry and bioeconomy. These issues among with environmental aspect are growing trends in mining industry and in society in general.

Scientists have suggested that there are promising biobased chemicals for mining industry, especially for concentration. Some of the biobased chemicals are promising alternatives for fossil-based chemicals, either fully or partly. However, further research is necessary in order to increase the use of biobased chemicals in mining industry.

Keywords: biobased chemicals, mining industry, fossil free

TIIVISTELMÄ

Biopohjaiset kemikaalit kaivosteollisuudessa

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Biopohjaiset kemikaalit, vihreä kemia ja biotalous ovat nousevia trendejä sekä kaivosteollisuudessa että yhteiskunnassa yleisesti. Tämä työ on kirjallisuuskatsaus, joka keskittyy biopohjaisten kemikaalien käyttömahdollisuuksiin kaivosteollisuudessa. Tavoitteena on erityisesti tarkastella biopohjaisia kemikaaleja, joiden on mahdollista korvata fossiilipohjaisia kemikaaleja osaprosesseissa. Kaivosteollisuudella on suuret vaikutukset ympäristöön, ja biopohjaiset kemikaalit ovat yksi mahdollisuus ympäristövaikutusten pienentämisessä.

Tutkijat ovat esittäneet, että jotkut biopohjaiset kemikaalit pystyisivät korvaamaan fossiilipohjaiset kemikaalit kaivosteollisuudessa, erityisesti rikastuskemikaaleina. Biopohjaiset kemikaalit pystyisivät toimimaan rikastuskemikaaleina yksinään tai seoksena kaupallisten fossiilipohjaisten kemikaalien kanssa, joten niiden käyttö on mahdollista myös teollisessa mittakaavassa. Lisätutkimusta kuitenkin vaaditaan, jotta biopohjaisista kemikaaleista saadaan pysyvä osa kaivosteollisuutta.

Avainsanat: biokemikaalit, kaivosteollisuus, fossiilivapaa

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1 INTRODUCTION

Mining industry is crucial for other industry fields as well as for humans directly. The growth of industrialization has increased the amount of annual output of metals and other mineral commodities (Wills 2006, p. 2). Mineral separation from the rock material needs to be economically viable. That is the reason for mineral separation process itself, and growth of technological improvements. The mineral sources are finite and technological improvements are the solution to mineral processing in the future. This includes, for example, improvements in concentration process and chemicals used in the process. (Wills 2006, p. 2)

Sustainability of industrial processes have become more important in recent years. Knowledge of environmental impact caused by mining industry have grown and at the same time green chemistry innovations have become a solid part of industry. Greenhouse gas emissions and even the physical footprint of mining industry is relatively small. For example, mining industry cause only 3% of the total CO_2 emissions of industrial field in Canada. (Dunbar 2016, p. 161) From this it is deduced that the keys to more sustainable mining and mineral processing are metal recycling and focusing on the replacement of hazardous chemicals used in the process with safer alternatives. Financial risks of new technologies adaptation in industrial scale are significant and this is one of the greatest challenges in the mining industry development. Mining industry is often considered as a slow innovator and mining industry is often forgotten in research. (Dunbar 2016, p. 185)

This thesis is a literature review, and the focus is on chemicals in concentration process and on new, biobased innovations. It is important to notice that environmental impact is not only the amount of green gas emissions. Industrial processes have potential to develop, not only by productivity but also by environmental impact. Novel applications of biobased materials are a growing field of research, and they may offer a solution to more sustainable mining industry.

2 UNIT PROCESSES

Mineral production process requires both mechanical and chemical activities. Minerals are underground and they are compounded to rock forming an ore. Mineral production process contains mining, comminution circuit, concentration, and dewatering. Mineral separation itself takes place in concentration process but all the stages before the concentration are equally important to ensure the best results. Concentration for example would be very inefficient without comminution circuit. Mineral production process might vary a bit, depending on the mineral. Common mineral production process is shown in Figure 1.

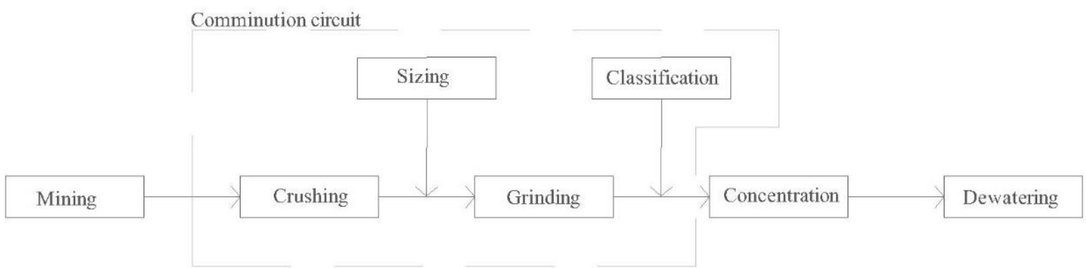

Figure 1: Mineral production process

2.1 Mining

The very first unit process in mineral production is mining. Valuable minerals form compounds with rock material, in other words, minerals and rock material form an ore. To exploit the valuable minerals, the ore must be extracted from the ground. This is called mining and there are two universally used methods: surface mining and underground mining. An open pit mine is a typical form of surface mining. A safe and functional open pit mine requires a high quality of engineering and operational ability. (Dunbar 2016, p. 37) Underground mining is a very complex process with many simultaneous sub-processes. The main difference between these two methods is that in surface mining the ore is extracted directly through the surface, in other words above the ore. Underground mining is executed inside the earth, and it requires mining tunnels, for example. Explosives are commonly used in both methods. Heavy machinery, such as trucks and dumpers, are used to help rock transportation. They need energy and fuel oil is commonly used energy source.

2.2 Comminution

2.2.1 Crushing and grinding

Crushing and grinding are used for three different purposes: to extract the valuable mineral from the ore, to increase reactive surface area, and to help transportation of ore particles during the process (Fuerstenau & Han 2003, p. 4). In this unit process, the particle size decreases. Different types of crushers and grinders, for example, jaw crushers and ball mills, are commonly used in this unit process. Usually more than one comminution equipment is needed to produce the preferred particle size. Comminution or grinding circuit is a term for a process where several crushers and grinders work in a row with classifiers to produce the preferred particle size. (Dunbar 2016, pp. 67, 70, 73, 75; Fuerstenau et al. 2003, p.94)

2.2.2 Sizing and classification

During the comminution process, the ore is sized and classified several times. Sizing and classification are crucial parts of the whole ore treatment process because many further operations require a specific particle size ratio to be effective. The sizing process can be fulfilled via classifiers and screens, for example. Classifiers are classified into four different groups: non-mechanical classifiers, mechanical classifiers, hydro cyclone classifiers, and pneumatic classifiers. Surface sorters and hydraulic classifiers are examples of non-mechanical classifiers, a spiral classifier is a mechanical classifier, and an air cyclone is a pneumatic classifier. (Fuerstenau et al. 2003, pp. 4, 149)

2.3 Concentration

2.3.1 Flotation

Flotation or froth flotation is a commonly used separation method for sulphide minerals. Mineral separation by flotation is based on the properties of the particle surface. Different chemicals, such as collectors and depressants are often used to increase flotation effectiveness. In the froth flotation process, the valuable mineral particles attach themselves to bubbles which causes mineral particles to rise with the bubble. The bubbles form a froth above the slurry, from where it is collected. Successful flotation requires hydrophobic mineral particles. Just a few minerals are naturally hydrophobic and that is why collectors are used. A collector is a chemical that adsorbs or coats the surface of the mineral particle and makes the surface of the mineral hydrophobic. Frothers and modifiers are also used to enable selective flotation. They either affect the hydrophobicity of mineral particles or decrease unwanted particle flotation. (Dunbar 2016, p. 77; Fuerstenau et al. 2003, pp. 245, 252)

2.3.2 Other concentration methods

In addition to froth flotation, concentration can be executed by gravity, magnetic force, or electrostatic force. In gravity concentration, particles with specific gravity are separated by gravitational or centrifugal force. In general, gravity concentration separates particles also by their size and shape. A shaking table is a typical application of gravity concentration. Magnetic concentration can be used for separating magnetic minerals (such as iron) from nonmagnetic minerals. In a magnetic separator, a drum rotates and magnetic particles flow over the drum attaching to its surface while nonmagnetic particles pass the drum. The surface of the drum is not itself magnetic but inside the drum is a stationary permanent magnet. Gravity force takes over the magnetic force at the bottom of the drum rotational path and the magnetic particles fall into a collection area. Electrostatic concentration is based on differences between the conductivity or surface charge of minerals. (Dunbar 2016, pp. 106, 109-110; Fuerstenau et al. 2003, pp. 4, 241)

2.4 Dewatering

Many unit processes in mining industry require water. Metal and water must be separated before further metal production. Thickeners, filters, and clarifiers are used to facilitate dewatering. Thickeners increase the solid content of process flow while clarifiers produce clearer water by removing suspended particles. Dewatering is usually accomplished in a large tank. The aim is that solid particles settle to the bottom. When the particles settle, the rotating rakes at the bottom of the tank force the solid particles into the underflow. Flocculant is generally added to slurry when it is fed to the tank. Flocculant accelerates the settling process by forming larger particles, flocs. Flocs settle faster than individual particles. (Dunbar 2016, p. 2016; Fuerstenau et al. 2003, pp. 5, 259)

3 CHEMICALS IN MINING INDUSTRY

The impact of mining industry activities to environment is invariable negative. In addition to mining itself, strong reagents in concentration process inflict a major risk to environment. Water contaminated with hazardous chemicals and disposal tailings are one of the most severe environmental risks in the field of mining industry. Waste treatment is often very expensive, and the image of the corporations is nowadays very important. Because of this, mining industry and corporations invest large amount of capital to improve their environmental impacts (Fuerstenau et al. 2003, p. 8).

3.1 Mining and comminution

Valuable mineral is liberated from gangue (non-valuable) minerals. The first step is to liberate ore fragment from bedrock. This is accomplished via blasting. Liberated ore fragments are transported from a mine to further processing. Depending on the size and hardness of the fragments, transportation is carried out via sluicing, belts, trucks, or individual blasting. (Wills 2006, p. 30) The most common explosives to accomplish blasting are ammonium nitrate fuel oil (ANFO) and emulsion explosives. More suitable option for underground blasting is emulsion explosives due to their higher velocity of detonation and lower critical diameter compared to ANFO explosives. (Zhang 2016, pp. 179, 181)

3.2 Concentration

Successful concentration requires different types of chemicals. Concentration via froth flotation is a common concentration method, especially in sulphide ore concentration (Wills 2006, p. 16). Chemicals in froth flotation are classified into three groups: collectors, frothers, and modifiers (regulators). The purpose of collectors is to increase the hydrophobicity of valuable mineral. The purpose of frother chemicals is to stabilize bubble formation and stabilize froth and therefore facilitate a good selectivity of the process. Modifiers modify the action of collector chemical which cause better selectivity towards valuable mineral(s). (Wills 2006, pp. 271, 276, 277)

3.2.1 Collectors

Collectors are classified into anionic and cationic collectors depending on type of their functional ion (Wills 2006, pp. 270, 271). Most of the collectors in mineral processing are anionic collectors. Anionic collectors can be oxyhydryl collectors or sulphydryl collectors. The efficiency of oxyhydryl collectors is based on their polar organic group or polar sulpho acid group. Commonly used chemicals in this group are fatty acids, sulphates, and sulphonates. Fatty acids, such as sodium oleate and linoleic acid, are good collectors for calcium, barium, magnesium, and non-ferrous metals. (Wills 2006, p. 272) Sulphates and sulphonates, such as lignosulphonates, are good collectors for barite, fluorite, apatite and scheelite. Sulphydryl collectors are used in sulphide mineral flotation, such as copper separation from galena (PbS). Sulphydryl collectors, mainly xanthates and dithiophosphates are the most used collector chemicals in mining industry. They are used as collectors of copper, gold, silver, oxidized minerals, and malachite. (Wills 2006, pp. 271-272, 275) Cationic collectors are not commonly used because of their great disadvantage: strict activity pH. However, cationic collectors, mainly amines are used for oxide, carbon, barite, or silicate flotation. Especially primary amines are strong collectors for apatite. (Wills 2006, p. 276; Nagaraj et al. 2014, p. 162) Examples of collectors are listed in Table 1.

Table 1: Commonly used collector chemicals.

Anionic collectors				
Type	Examples	Advantages	Disadvantages	Reference
Oxyhydryl: Fatty acids, sulphates, and sulphonates	Sodium oleate, linoleic acid lignosulphonate, alkyl sulphate	Fatty acids have a strong collecting power. Sulphates and sulphonates demonstrate better selectivity than fatty acids.	Fatty acids demonstrate a low selectivity. Sulphates and sulphonates are not as strong collectors as fatty acids.	Wills 2006, pp. 271-272; Fuerstenau 2003, p.253.
Sulphydryl: xanthates, dithiophosphates	Sodium ethyl xanthate, isopropyl thiocarbanate	Powerful and selective collector	Very hazardous. Effective oxidized mineral flotation requires great doses of sulphydryl collector.	Wills 2006, pp. 271-272, 275.
Cationic collectors				
Type	Examples	Advantages	Disadvantages	Reference
Cationic	Napthylamine diaminobenzene	Primary amines are good collectors for apatite. Primary amines are able to ease the flotation of sedimentary phosphates from calcareous ores.	Very pH-sensitive, weak collecting power	Wills 2006, p. 276; Nagaraj et al. 2014, p. 162.

3.2.2 Frothers

Frother chemical(s) are the base of a good selectivity of froth flotation. Frother chemical stabilize bubble formation and therefore cause a stable froth. Stable froth is necessary for good selectivity. Stable froth increases flotation kinetics as well. (Wills 2006, p. 276) In general, substances with hydroxyl-, carboxyl-, carbonyl-, amino-, or sulpho group are conceivable frothers. Chemical properties of many frothers are similar with ionic collectors. (Wills 2006, pp. 276-277) Alcohols are the most universally used frother chemicals because they do not possess collector properties. Pine oil, which contains aromatic alcohols, is commonly used as well as cresylic acid. (Wills 2006, p.277) Synthetic frothers based on high molecular weight alcohols are in common use nowadays. Their advantage comparing to pine oil and cresylic acid is easier process controlling. Amines are also commonly used frother chemicals due to their low collective properties. Simultaneous frother and collector properties of reagent hinder selective flotation. However, acids are sometimes used as a frother despite their carboxyl group which causes a strong collector ability of reagent as well. (Wills 2006, pp. 277) Commonly used frother chemicals are listed in Table 2.

Table 2: Commonly used frother chemicals.

Reagent	Target mineral	Reference
Pine Oil	Sulphide minerals	Wills 2006, p. 277; Michaud 2016.
Cresylic acid	Lead sulphide (PbS)	Wills 2006, p.277.
Methyl isobutyl carbinol (MIBC)	Graphite, coal, lithium, mica, barite,	Wills 2006, p. 277; Bulatovic 2015, pp. 46, 133, 164, 192,
Eucalyptus oil	Sulphide minerals, replacement of pine oil.	Michaud 2015; Michaud 2016.
Polyglycol ethers	Carbonaceous copper, quartz	Wills 2006, p. 277; Kowalczuk et al. 2014.
Polypropylene glycol ethers	Copper, lead, nickel and zink	Nagaraj et al. 2014, p. 160 Crozier 1992, p.85
Alkoxy-paraffins	Copper, lead, nickel and zink	Nagaraj et al. 2014, p. 160 Crozier 1992, p. 98.

3.2.3 Modifiers

Modifiers, also known as regulators, are reagents which modify the action of the collector. Modifiers are classified into three types, depending on their action method: activators, depressants, and pH modifiers. (Wills 2006, p. 277) Activators cause hydrophobicity of wanted mineral. Usually, activators are soluble salts. (Wills 2006, p. 278) Depressants render unwanted hydrophilic minerals by restricting their flotation. Depressants are the key to selective flotation and therefore economical process. Depression is more difficult to control than other types of modifiers due to lack of full knowledge of functioning of depressants (Wills 2006, p. 279). Commonly used activator chemicals are listed in table 3 and commonly used depressant chemicals are listed in table 4.

Table 3: Commonly used activator chemicals.

Reagent	Target mineral	Reference
Copper sulphate	Sphalerite [(Zn, Fe)S], Arsenopyrite (FeAsS), Galena, Calcite, Pyrite	Wills 2006, p. 278; Michaud 2016
Lead nitrate	silicates, sodium chlorite	Michaud 2016; Crozier 1992, p. 103
Sodium (hydro)sulphide	Cerussite, malachite	Wills 2006, p. 278.

Table 4: Commonly used depressant chemicals.

Reagent	Target mineral	Reference
(Sodium)cyanide	Sphalerite, pyrite, copper sulphites	Wills 2006, p. 279.
Zink sulphate	Sphalerite	Wills 2006, p. 280
Lime	Pyrite, galena, cobalt sulphides	Crozier 1992, p. 104
Sulphur dioxide, Potassium dichromate	Galena	Wills 2006, p. 281
Dextrin	Gangue minerals, talc, graphite, graphite, calcite, lead	Nagaraj et al. 2014, p.164; Wills 2006, p. 281
Tannin and tannic acid	Gangue minerals, talc, graphite, graphite, calcite	Nagaraj et al. 2014, p. 164; Michaud 2016; Wills 2006, p. 281
Starch	Gangue minerals, talc, graphite, graphite, calcite, lead	Nagaraj et al. 2014, p. 164; Wills 2006, p. 281
Carboxymethyl cellulose (CMC), guar	Talcaeous gangue minerals	Wills 2006, p. 281.

3.3 Dewatering

Usually mineral liberation, especially flotation, is accomplished with a significant amount of water. Solids and water must be separated from each other to produce metal effectively. Thickeners and filters are the most common ways to accomplish dewatering. (Fuerstenau et al. 2003, p. 5) Chemicals called flocculants are usually added to accelerate sedimentation of solid particles. Inorganic salts and lime are common flocculants. (Fuerstenau et al. 2003, p.317; Wills, 2006 p. 379)

4 BIOBASED CHEMICALS

4.1 Flotation

Many chemicals in mineral flotation are toxic and fossil-based and as a result, they cause environmental issues. Scientists have demonstrated that effective froth flotation unit processes are possible with biobased chemicals. Biobased chemicals may replace commercial chemicals totally or partially and therefore the environmental impact of the froth flotation process decreases.

4.1.1 Collectors

Lignin micro- and nanoparticles are alternatives to xanthates in the flotation process. Lignin micro- and nanoparticles are able to replace xanthates totally or partially as a depressant chemical. Especially organosolv lignin made of spruce or birch has demonstrated a potential replacement for fossil-based collectors. In copper-nickel ore flotation, lignin particles are selective towards copper. Recovery of iron is poor with lignin-based collectors. Poor iron recovery decreases usage of chemical in further enrichment process because iron is a non-preferred mineral. Comparing to synthetic chemicals, this attribute is also an advantage. In nickel flotation lignin-based collector is feasible only with presence of activator. With lignin-based collector and activator the grade of nickel is up to 2.5 times higher than with xanthate. Activator usage increases copper grade and recovery but simultaneously recovery of iron. Nevertheless, the iron recovery remains lower than with xanthate. (Hrůzová et al. 2020, pp. 2-3) In zinc-lead-copper ore froth flotation, lignin-based chemicals demonstrated selectivity to lead instead of copper. This is not preferred ability; however, lignin collectors can partially (up to 50%) replace xanthates. This decreases fossil-based chemical requirement in froth flotation. (Hrůzova et al. 2020, p. 3)

Other cellulose derivatives have also potential collector properties. Cellulose is easy to manipulate and synthetize with other substances for example by attaching hydrophobic alkyl chains. (Laitinen et al. 2016, p. 261) Aminated nanocelluloses demonstrate a good selectivity towards quartz and alumina. Longer chains, primarily n-hexyl, n-pentyl or nbutyl aminated cellulose (HAC, PEAC and BAC) demonstrate better selectivity and recovery of quartz than aminated cellulose with shorter chains. The reason for that is the dependence between quartz flotation efficiency and the hydrophobicity of collector, in this case aminated nanocellulose. (Laitinen et al. 2016, p. 264) Experiments by Laitinen et al. (2016) was accomplished with pure quartz and alumina. Minerals are with ore in industrial scale. Aminated nanocellulose requires more investigation as a collector, although the results were promising.

Vegetable oils, for example macauba pulp oil and jatropha curcas oil have demonstrated potential as a biobased collector. In pH range 8-10, the recovery of apatite is over 90%, similar with macauba pulp oil and jatropha curcas oil. (Zhang et al. 2019, pp. 38, 43-44) Potential biobased collector chemicals are listed in Table 5.

Table 5: Potential biobased collector chemicals.

Biobased chemical	Application (ore)	Efficiency	Conclusion	Reference
Organosolv spruce lignin microparticles (SM)	Copper (copper-nickel) Lead, copper (zink-lead-copper)	87% recovery, 8.9% grade poor	SM is able to replace xanthates totally or partially.	Hrůzova et al. 2020, pp. 2-3.
Organosolv birch lignin microparticles (BM)	Copper (copper-nickel) Lead, copper (zink-lead-copper)	70% recovery, 8.6% grade poor	BM is able to replace xanthates totally or partially.	Hrůzova et al. 2020, pp. 2-3.
Organosolv birch lignin nanoparticles (BN)	Copper (copper-nickel) Lead, copper (zink-lead-copper)	77% recovery, 7.9% grade poor	BN is able to replace xanthates totally or partially.	Hrůzova et al. 2020, pp. 2-3.
Long-chain alkyl aminated cellulose (HAC, PEAC and BAC)	Quartz	HAC and PEAC cause approximately 93%-95% quartz recovery in pH range 6-9. PEAC and BAC cause approximately 90% quartz recovery in pH 10. BAC cause 70%-75% quartz recovery in pH range 6-9.	HAC, PEAC and BAC are potential biobased collector for quartz.	Laitinen et al. 2016, p. 263.
Macauba pulp oil	Apatite (fluorapatite)	over 90% recovery in pH range 8-10.	Macauba pulp oil is a good alternative to replace synthetic fatty acids.	Zhang et al. 2019, pp. 43-44.
Jatropha curcas oil	Apatite (fluorapatite)	In pH 10 with high dosage recovery is up to 96.8%.	Jatropha curcas oil is potential biobased collector chemical	Zhang et al. 2019, p. 44.
Mixture of humic acid (HA) and commercial collector	Copper (copper sulphide)	Recovery up to 80.64% Faster than commercial collector alone	HA is able to partially replace synthetic collectors.	Reyes-Bozo et al. 2019, p. 5.

4.1.2 Depressants

Different acids have a strong potential as depressants in the froth flotation process. Acid manufacturing from biobased resources is already in use. The froth flotation process requires usually high doses of inorganic depressants. Depression of undesirable minerals is a crucial unit process in successful froth flotation. One of the most potential innovations in this area is polyglutamic acid (PGA) which is polymerized amino acid. PGA is a good pyrite depressant and the impact for chalcopyrite recovery is insignificant. Proper action of depressant is necessary to effective flotation. Effectiveness is lower if the depressant decreases the recovery of valuable mineral. (Khoso et al. 2019) PGA is able to function at lower pH than a commonly used depressant chemical, lime (Khoso et al. 2019). Another potential amino acid depressant is L-cysteine. L-cysteine demonstrates an excellent separation between molybdenite (MoS_2) and galena (PbS) in pH range 6-9. Commonly used depressants in Mo-Pb froth flotation are sodium sulphide, sodium hydrosulphide or sodiumthiophosphate (Nokes' reagent). These substances are highly toxic, and their usage causes environmental issues. (Yin et al 2019, pp. 177, 179)

Additionally, biobased chemicals have proven effects in rare earth element (REE) flotation. The study of Wang et al. (2020) demonstrates that xanthan gum is able to depress calcite in bastnaesite-calcite ($(REE)FCO_3$-$CaCO_3$) flotation. Bastnaesite and calcite have similar surface characteristics. Similar surface characteristics cause similar recoveries and therefore poor separation effectiveness. Xanthan gum is able to depress calcite recovery by 85.09% and bastnaesite recovery by 22.37%. The difference between the recoveries after using xanthan gum as a depressant indicates that bastnaesite separation is possible. (Wang et al. 2020, pp.1, 8)

Nowadays, applications of starches are used as depressants in froth flotation. Soluble starch has more applications in industry than other starches. However, Kar et al. (2013) demonstrated that in cationic flotation corn starch, potato starch, and rice starch have similar efficiencies as a hematite depressant as soluble starch has. Likewise starches, other polysaccharide derivatives have demonstrated promising results as depressants. For example, pectin is able to depress calcite in scheelite-calcite separation (Jiao et al. 2019, p. 1). Some monosaccharides have also depressive characteristics. Castillo et al. (2020)

have demonstrated hemicellulose-based monosaccharides as molybdenite depressants. D-mannose and D-glucose have the strongest depressive effect due to their molecule structure: D-mannose and D-glucose have more carbon atoms and hydroxyl groups than other monosaccharides. More carbon atoms and hydroxyl groups allow more interactions between monosaccharide depressant and molybdenite. (Castillo et al. 2020, pp. 758, 764). Potential biobased depressants are listed in Table 6.

Table 6: Potential biobased depresser chemicals

Biobased chemical	Application	Effiency	Conclusion	Reference
Polyglutamic acid (PGA)	Pyrite depression (chalcopyrite flotation)	85% copper recovery in pH range 8-12	PGA is a potential biobased solution to replace lime as a depressant.	Khoso et al. 2019, p. 895.
L-cysteine	Galena depression (molybdenite flotation)	Possible when pH-range is 6-9.	L-cysteine is an effective alternative depressant in molybdenite flotation.	Yin et al. 2019, p.179.
Xanthan gum	Calcite depression (bastnaesite flotation)	Effective in pH 8.	XG has a strong potential as a biobased depressant.	Wang et al. 2020, p. 8.
Starch	Hematite depression (iron ore)	85-85% iron recovery 63-65% iron grade	Starches are already used as a depressant.	Kar et al. 2005.
Monosacchari des	Molybdenite depression	Molybdenite flotation is approximately 60% at the lowest, monosacchari-des are more effective in high pH.	Monosaccharides, especially D-mannose and D-glucose are potential biobased depressants.	Castillo et al. 2020, p. 760.
Galactogluco mannan hemicellulose (HC)	Molybdenum and clay mineral depression (for example kaolinite) in copper flotation	7,6% higher copper recovery than without HC. Molybdenum recovery is 20,7% less than without HC.	HC is potential depressant in copper flotation if ore does not contain molybdenum.	Hernandez et al. 2017, pp. 198, 200.

4.1.3 Frothers

Biobased frothers have a strong potential to decrease the environmental impact of froth flotation and the whole ore treatment process but there are only a few reliable studies in this field. However, efficiency of a mixture of commercial frother and biodegradable amphiphilic polymer, hydroxypropyl methyl cellulose (HPMC), have been demonstrated. This type of mixture is also known as polymer-surfactant mixture (PS-mixture). Efficiency of HPMC as a frother alone is also demonstrated. PS-mixture demonstrates effective and selective copper flotation from chalcopyrite or copper-rich tailings. Grade, recovery, and selectivity towards copper are approximately same as with commercial frother alone. PS-mixture demonstrates faster kinetics than with commercial frother alone. (Nuorivaraa & Serna-Guerrero 2020, pp. 2-5, 7, 9) This mixture has an excellent adaptation ability to process circumstance changes, for instance, pH changes or collector chemical concentration changes. Thus, amphiphilic cellulose mixture is able to decrease the necessity of hazardous chemicals by replacing commercial frother chemicals. Furthermore, HPMC-mixture facilitates flotation of low hydrophobicity minerals and therefore renders copper flotation from copper-rich tailings possible. (Nuorivaara & Serna-Guerrero 2020, p. 6-7)

4.2 Dewatering

Usage of dewatering chemicals, inorganic salts, or synthetic polymers have three great disadvantages: metal concentration in water increases, risk of health hazard through dispersion of acrylamide oligomers, and remarkable amount of sludge. Sludge might be toxic depending on the used chemicals due to which sludge is not only challenge for waste treatment but also environmental and health risk. (Renault et al. 2009, p. 1338) Biopolymers are economic, environmental-friendly, and they have low toxicity. Due to these characteristics, growing interest in biopolymers as flocculants is to be expected. Chitosan is one of the promising bioflocculants. It is prepared from chitin which is a common polysaccharide in nature. (Renault et al. 2009, pp. 1337, 1338) Chitosan has two disadvantages: it has low solubility in water, and it is very sensitive to changes in pH. Flocculation of kaolinite via chitosan is the most effective in the narrow vicinity of pH 7. (Yang et al. 2014, p. 480; Divakaran et al. 2004, p. 2138) Chemical modifying of chitosan improves these characteristics and its possibilities as a bioflocculant. For example, chitosan-graft-poly[(2-methacryloyloxyethyl) trimethyl ammonium chloride] also known as CMC-g-PDMC has even better flocculant properties towards kaolin than commercially used flocculant polyaluminium chloride, PAC. Moreover, CMC-g-PDMC dosages were significantly lower (0,15-0,80 mg/l) than dosage of PAC (4-20 mg/l). (Yang et al. 2014, p. 485)

5 SUMMARY AND DISCUSSION

It is obvious that the mining industry needs solutions towards more environmental-friendly and sustainable actions. Biobased chemicals have a potential to be a part of this transition. Some biobased chemicals, such as organosolv spruce lignin microparticles or xanthan gum, are alternatives to fully replace fossil-based chemicals. Dosages of chemicals in mining industry, especially in concentration process, are significant. Thus, it makes impact even if chemicals are partially replaced with biobased alternatives. Mixtures with commercial used non-biobased chemical and biobased chemical have approximately same properties and advantages than non-biobased chemical alone. Biobased chemicals are a step to a better direction not only because many chemicals and their manufacturing process are harmful to the environment but also because their natural origin does not set special requirements to wastewater handling. The preparation process of many biobased chemicals includes high degree of modifying the natural resource; therefore, the biodegradability of biobased chemicals needs further research and knowledge.

Biobased chemicals have potential but there are also challenges. One of the biggest issues is the lack of research in industrial scale. Results of the bench-scale research experiments are promising but it might be challenging to transfer the biobased chemical dosages and optimal reaction circumstances into industrial scale production process. Mining industry does not develop fast and leading the way towards sustainable mining industry via biobased chemicals might not be the priority of companies. According to my knowledge and own experience, reusing side streams and wastes, such as gangue, are more common actions to minimize negative environmental impact. Furthermore, it is not proven that all chemicals in all concentration unit processes are feasible. The lack of data concerning how different biobased chemicals work together might lead to a situation where the concentration process with biobased chemicals might not be as effective as the concentration process with (partially) non-biobased chemicals.

The availability of biobased chemicals might be challenging as well. For example, promising biobased collector, organosolv spruce microparticles (SM), is manufactured from a side stream of organosolv pulp process. Organosolv pulp process is not the most common pulp manufacturing process. This might cause challenges to gain enough SM for industrial collector. Challenge is similar with many other biobased chemicals: they are derivates from natural resources. Is it feasible or ethical to manipulate resources to get biobased chemical? For example, many starches are derived from food crops.

Biobased chemicals have potential in mining industry. Some biobased chemicals, such as organosolv spruce lignin microparticles, long-chain alkyl aminated cellulose, polyglutamic acid and xanthan gum are biobased alternatives to fully replace fossil-based chemicals. They are effective and more environmentally friendly than fossil-based or synthetic chemicals. The main interest is to decrease the negative environmental impact of mining industry, especially impact of flotation chemicals. All biobased chemicals might not be able to fully replace synthetic chemicals, but mixtures of commercially used, non-biobased chemical and biobased chemical are step to a better direction. In fact, flotation reagent mixtures with approximately same properties as commercial chemicals alone demonstrate faster kinetics than with commercial chemical alone. Biobased chemicals are easy to recycle and waste water with biobased chemicals does not require as much treatment chemicals as wastewater with synthetic chemicals such as xanthates. Comparison of advantages and challenges of both biobased and non-biobased chemical are shown in Table 7.

Table 7: Comparison of biobased and non-biobased chemicals.

	Biobased chemical	Non-biobased chemical
Advantages	Decreases environmental impact Natural resource Easier wastewater handling	Commercially used for years, even decades Process development is based on commercially used chemicals
Challenges	Accessibility Ethical aspect of the resource Lack of scientific data in industrial scale production; not universal	Usually fossil-based and not renewable Harmful to environment and humans; sets requirements for wastewater handling

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