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## Shades of green: the path to flotation reagents development

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Despite growing interest in eco-friendly reagents for mineral processing, a standardized definition for green products in flotation operations remains absent. This study proposes a comprehensive classification framework for flotation reagents, grounded in four key pillars: safer chemical profiles, biodegradability, sustainable raw materials, and green production. These pillars are ranked by relevance and integrated into a scoring system ranging from 0% to 100% green, applicable to the major flotation reagent categories: collectors, depressants, and frothers. The framework facilitates a more comprehensive assessment of current reagent sustainability and identifies areas for improvement. By establishing a chemistry-based benchmark with the materials used for flotation today, this work supports the development of next-generation reagents aligned with environmental and safety goals, contributing to more sustainable beneficiation practices.

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### Green foundation

1. Flotation reagent development has been discussed in the context of green chemistry principles.
2. The area gains importance considering there is an increasing need for critical minerals worldwide, and flotation is one of the most important operations in mineral processing.
3. The purpose of this article is to help the mineral processors and researchers in the area of mining and mineral processing to look for better and more sustainable reagents to apply to their operations. The main point is to also include the sustainability of the chemicals as an important step in the development, besides reagent performance.

## Introduction

Chemical reagents are key in mineral flotation processes, for both selectivity and recovery, since they are essential parameters related to performance and process sustainability. As flotation is one of the most applied concentration techniques worldwide, some challenges arise towards the evolution of this operation unit application, such as fine and coarse particle recovery, excessive slime presence, variable ore composition and how to handle it, water use and its quality, toxicity of the reagents, and high operation costs. Water use and reagent application are closely related in the mining industry. Around 1–2% of fresh water consumed is destined for mining operations in some countries such as Brazil, the United States, and Australia.<sup>1–3</sup> This percentage may increase depending on the intensity of the mining activities in the country in relation to

other water-consuming activities.<sup>4</sup> Flotation demands the greatest amount of water in mineral processing plants, requiring 3–7 t of water for 1 t of ore treated.<sup>5</sup> Reusing and/or recirculating process water reduces costs and environmental risks related to the discharge of wastewater into the surrounding areas.<sup>5</sup> In some cases, the consumption of reagents can be diminished by half when water is recirculated, making the process more efficient.<sup>6</sup>

However, chemical reagents are typically petroleum-derived and produced *via* traditional processes, presenting high toxicity and sometimes being non-biodegradable (cumulative). Therefore, application demands cost savings and regulations that favor the growth of green chemistry (GC) in global markets, including the mining industry.<sup>7</sup> Large companies in developed markets have, for the most part, implemented GC strategies, but this is not the case for smaller companies and mines in developing countries, such as India and China.<sup>7</sup> This is a reflex of the fact that GC and sustainability are intertwined with the social and political structure of the countries and cannot be discussed/analyzed in isolation.<sup>8</sup> The geopolitical situation also contributes to companies developing various

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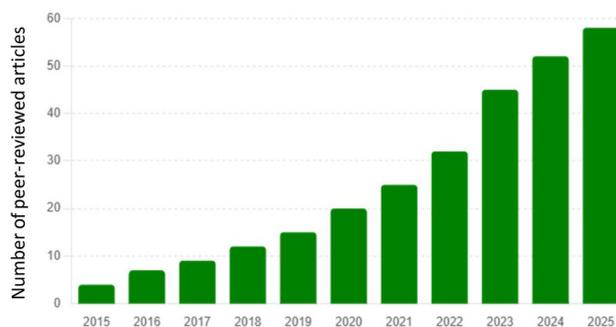
strategies to keep their processes running smoothly. One important example is that the energy crisis in heavily industrialized European countries may increase the sustainability of green chemicals, creating a unique opportunity to shift towards greener production technologies.<sup>9</sup> Another example is the war between Israel and Iran, where Iran announced that it may close the Strait of Hormuz, directly impacting the petroleum distribution and, consequently, raising prices of all petroleum-derived chemicals and affecting the markets.<sup>10</sup>

Flotation reagents (collectors, depressants, frothers, activators, *etc.*) are chemicals used to enhance the selective separation of valuable minerals from the rest of the ore. As many of them are traditional reagents, ecotoxicity tests show that they adversely impact water quality, aquatic organisms, and soil health. Biodegradation studies indicated that some synthetic flotation reagents persist in the environment, exacerbating their toxic effects.<sup>11</sup> Xanthates, dithiophosphates, and amines are commonly used in the flotation process. Xanthates, as the most common collectors in sulfide flotation, can decompose into carbon disulfide (CS<sub>2</sub>), representing a health hazard. They have significant aquatic toxicity, negatively affecting fish and microorganisms due to their persistence and bioaccumulation potential.<sup>12,13</sup> Amines are toxic to marine life and pose risks to ecosystems due to their surfactant properties.<sup>11</sup> Synthetic depressants like sodium cyanide, often used in sulfide mineral flotation, are highly toxic, posing severe environmental and human health risks.<sup>14</sup> Moreover, MIBC (methyl isobutyl carbinol), as the most well-known frother, is reported to exhibit moderate toxicity to aquatic organisms.<sup>15</sup>

In response to stricter environmental regulations and sustainability goals in the mining industry, and also different environmental policies in many countries such as Dual Carbon in China and the EU Green Deal, among others, there has been a growing drive to develop “green” flotation reagents that are biodegradable and less harmful. These green reagents are designed to minimize ecological impact while maintaining metallurgical performance. Over the past decade, research interest in environmentally benign reagents has increased markedly, reflecting a broader trend toward sustainable mineral processing practices (Fig. 1). Early research in the

mid-2010s mostly explored a few natural reagents (*e.g.*, plant-based depressants or biosurfactants) as case studies. As environmental sustainability became a core consideration, funding and interest in this topic expanded. By the 2020s, multiple avenues, from biodegradable polymers for mineral depression to biobased collectors, are being actively studied, as reflected by the surge in research publications. The bibliometric trend also suggests that the research community and industry stakeholders are increasingly prioritizing greener chemistries for mineral processing. This corresponds to stricter regulations (for instance, bans on certain toxic chemicals) and industry initiatives to reduce the environmental footprint of mining.

In this context, an eco-friendly reagent is a material that aligns with the main principles of green chemistry, considering its production and application, which can be summarized in four main pillars: biobased raw materials, green production, safer chemicals, and biodegradability.<sup>16</sup> However, the main question is “How can a reagent be classified as green?” So far, the evaluation system built to assess flotation collectors has only considered the information contained in the Safety Data Sheet (SDS), including physical and chemical hazards, stability and reactivity, as well as environmental and health impacts.<sup>17</sup> It is important to acknowledge the limitations of an only SDS-based evaluation, because it means that systems like this consider only a simplified application of the product, but not its full complexity of hazard assessment in the development and production phases. Most published scientific reports did not provide evidence or facts to highlight how their reagents were classified as green. They frequently mentioned the renewable origin (*e.g.*, plant starch, cellulose, tannins, and vegetable oils) of reagents and biodegradability, leading to lower environmental persistence. The researchers typically compared the ecotoxicological profiles of biobased reagents with those of synthetic ones. It is generally indicated that the biobased alternatives commonly exhibit significantly lower aquatic toxicity, less harm to soil microbiota, and safer handling properties. This assumption can also lead to reagent choices where the material is natural but still toxic.<sup>8</sup> Thus, the suggestion for replacing or significantly reducing conventional toxic flotation reagents with naturally derived materials was based on just the assumption of inherently lower toxicity. In other words, reports about green flotation reagents rely predominantly on assumptions of environmental benefits regarding biodegradability and renewability. Only a few studies have considered ecotoxicological studies and Life Cycle Assessments (LCAs) regarding the newly developed flotation reagents, which claim to be green. Therefore, it would be essential to establish a structure for such a drawback and explain what can be called a green flotation reagent. To address these essential gaps, this article presents a multidisciplinary overview of green flotation reagents through the analysis of different documents (SDS, articles and patents), offering a vision that a range of stakeholders (researchers, chemical, and mining companies) must share to enhance the sustainability of the process from a broad perspective.



**Fig. 1** The approximate trend in the number of peer-reviewed scientific articles published on green and eco-friendly flotation reagents from 2015 to 2025.



## Green chemistry

Anastas & Warner (1998) suggested that green chemistry can be defined according to 12 principles (P) summarized as follows: (P1) prevention of waste; (P2) atom economy (AE) or maximization of all materials into the final product; (P3) wherever practicable, design less hazardous chemical synthesis; (P4) design of safer chemicals; (P5) avoidance or application of safer solvents and auxiliaries, (P6) energy efficiency (ambient temperature and pressure, whenever possible); (P7) use of renewable feedstocks, whenever practicable; (P8) reducing derivatives; (P9) catalysis; (P10) biodegradation of products; (P11) real-time analytical chemistry; and (P12) accident prevention.<sup>18,19</sup> Those principles are related to economic, human, and environmental concerns, fitting into the sustainable development of society. In this context, a green flotation reagent can be defined based on the green chemistry concept, which has four main tiers (Fig. 2): safer chemicals (P4), biodegradability (P10), biobased raw materials (P7), and green process (P1, P2, P3, P5, P6, P8, P9, P11, and P12).

### Safer chemicals

The application of safer chemicals is the most important criterion for a reagent to be considered green since safety is immediate and non-negotiable. A reagent that is biodegradable but highly toxic is still dangerous during its active life and can cause harm before it degrades. The safety of a reagent can be divided into physical hazards and toxicity to humans and ecosystems.

**Physical hazards.** Physical hazards, such as explosives, flammable liquids and solids, self-reactive substances and mixtures,

among others, pose risks during transport, storage, and use, therefore should be strongly avoided as flotation reagents. In this category, flammable liquids (having a flash point of not more than 93 °C) are one of the most studied characteristics (Table 1). Frothers may fit into the flammable category, such as MIBC, and the main challenge some companies face is to increase the flash point of the different frothers, so the final product can be safer and fit into category 4 of combustible liquids (Table 1). This practice supports increasing the safety in the mining industry application.<sup>20</sup> Corrosiveness to metals can also be considered a physical hazard. However, for many flotation reagents, the reactivity associated with adsorption onto a metal surface is closely related to their corrosive properties. Thus, the corrosive nature of a reagent cannot simply be disregarded.

**Toxicology concepts and definition.** Too much of anything can kill, according to Paracelsus.<sup>21</sup> It means that the toxicity of a compound is correlated with its dosage and type.<sup>22</sup> A chemical is toxic if it can produce a toxic effect in an organism, which can be of various kinds, such as local and systemic, reversible and irreversible, immediate and delayed impacts.<sup>22,23</sup> Additionally, the idea that natural compounds may be safer than synthetic ones is a misconception, considering that there are many different extremely potent biologically natural substances.<sup>8</sup>

“Green toxicology” is a concept that integrates principles of toxicology into the goal of designing safer chemicals to minimize potential toxicity in early stages of chemical development.<sup>24</sup> The benign design concept is one of the principles of green toxicology and is linked to the knowledge of different structures or substructures, whose presence may indicate certain adverse effects.<sup>25</sup> They are informative and can be identified by computational methods, which strengthens and supports the development of safer compounds.<sup>25,26</sup> The application of determined chemical substances depends on the different chemical regulations of the countries (for instance, REACH in Europe, TSCA in the United States, AICIS in Australia, the IECSC in China and also the MEE order 12, among others) and countries that produce certain chemicals. It means that a substance that is produced and applied in one country cannot necessarily be made and/or used in another one. Countries with chemical regulations in place typically have stronger regulatory measures and are much stringent regarding different chemical applications. From a practical perspective and for a better understanding of toxicity, it can be divided mainly into human and environmental hazards.

**Human hazards.** The UN Globally Harmonized System (GHS) Purple Book brings the information about the “Globally

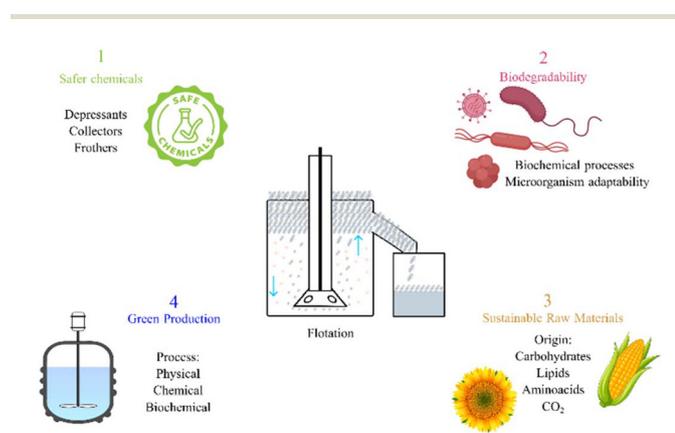


Fig. 2 The four concepts to define a green flotation reagent.

Table 1 Criteria for flammable liquids<sup>20</sup>

Cat.	Criteria	Symbol	Signal word	Hazard statement
1	Flash point <23 °C and initial boiling point ≤35 °C	Flame	Danger	Extremely flammable liquid and vapour
2	Flash point <23 °C and initial boiling point >35 °C	Flame	Danger	Highly flammable liquid and vapour
3	Flash point ≥23 °C and ≤60 °C	Flame	Warning	Flammable liquid and vapour
4	Flash point >60 °C and ≤93 °C	No symbol	Warning	Combustible liquid



Harmonized System of Chemicals". It refers to acute toxicity as "serious adverse health effects (*i.e.*, lethality) occurring after a single or short-term oral, dermal or inhalation exposure to a substance or mixture".<sup>20</sup> The acute toxic effect can manifest immediately after exposure to a toxic compound and can be evaluated through a test known as LD<sub>50</sub> "Lethal Dose" (oral, dermal) or LC<sub>50</sub> "Lethal Concentration" (inhalation), which determines the minimal lethal dosage to kill half of the animals exposed.<sup>20,23,27</sup> Thus, the values may be expressed as acute toxicity estimates (ATEs) (Table 2). In ATEs, Category 1 is the highest hazard category, while Category 5 is for substances with relatively low acute toxicity, which, under certain circumstances, may offer a hazard to vulnerable populations.<sup>20</sup>

The chronic effect may occur after prolonged exposure to a substance that has accumulated in the organism over several years, finally reaching a concentration at which the toxic effect occurs. The chronic impact can also refer to persistent damage over an extended period, which occurs due to cut poisoning.<sup>23</sup> Extensive testing may be necessary for a 2-year chronic toxicity study in rats or mice, looking for apparent signs of toxicity (example: liver failure and kidney cancer).<sup>27</sup> Therefore, from the "human hazard" perspective, a flotation reagent can be classified as green if it meets the following criteria related to acute toxicity: belongs at least to Category-4 based on the GHS. Specifically, it must have: oral toxicity (LD<sub>50</sub>) between 300 and 2000 mg per kg body weight. Dermal toxicity (LD<sub>50</sub>) is between 1000 and 2000 mg per kg body weight. Inhalation (dusts and mists) toxicity (LC<sub>50</sub>) between 1.0 and 5.0 mg L<sup>-1</sup>. Additionally, it should not display significant chronic toxicity, meaning that it does not cause substantial damage after prolonged exposure or accumulate in the organism, causing persistent harm (*e.g.*, liver damage and carcinogenicity).

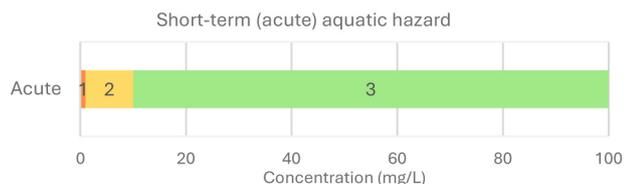
**Environmental hazards.** The environmental hazard is measured by acute aquatic toxicity, meaning that the intrinsic property of a substance is injurious to an organism in a short-term aquatic exposure to that substance.<sup>20</sup> The acute aquatic toxicity would typically be determined using a fish, a crustacean species, and/or an algal species, which are considered surrogates for all aquatic organisms.<sup>20</sup> In general, for short-term aquatic hazards, there are 3 categories for fish (96 h), crustaceans (48 h), and algae or other aquatic plants (72 h/96 h). Acute 1 presents a "Lethal (or Effective) Concentration" L(E)C50 ≤ 0.1 mg L<sup>-1</sup>; acute 2, 1 mg L<sup>-1</sup> < L(E)C50 ≤ 10 mg L<sup>-1</sup>; and acute 3, 10 mg L<sup>-1</sup> < L(E)C50 ≤ 100 mg L<sup>-1</sup> (Fig. 3).

In general, aquatic toxicity and bioaccumulation can be avoided if the substance degrades rapidly in the environment, increasing the importance of the biodegradability of the different substances. Thus, to classify a flotation reagent as green based on the "environmental hazards" perspective (specifically aquatic toxicity and biodegradability), it should ideally have a very low intrinsic toxicity level toward aquatic organisms (fish, crustaceans, and algae) upon short-term exposure at environmentally realistic concentrations. The flotation reagent should not accumulate significantly in aquatic organisms, thus avoiding long-term chronic effects.

**Table 2** ATE values and criteria for human acute toxicity hazard categories (Cat.)<sup>20</sup>

Exposure route	Cat. 1	Cat. 2	Cat. 3	Cat. 4	Cat. 5
Oral (mg per kg bodyweight)	ATE ≤ 5	5 < ATE ≤ 50	50 < ATE ≤ 300	300 < ATE ≤ 2000	2000 < ATE ≤ 5000
Dermal (mg per kg bodyweight)	ATE ≤ 50	50 < ATE ≤ 200	200 < ATE ≤ 1000	1000 < ATE ≤ 2000	—
Gases (ppmV)	ATE ≤ 100	100 < ATE ≤ 500	500 < ATE ≤ 2500	2500 < ATE ≤ 20000	—
Vapors (mg L <sup>-1</sup> )	ATE ≤ 0.5	0.5 < ATE ≤ 2.0	2.0 < ATE ≤ 10.0	10.0 < ATE ≤ 20.0	—
Dust and Mist (mg L <sup>-1</sup> )	ATE ≤ 0.05	0.05 < ATE ≤ 0.5	0.5 < ATE ≤ 1.0	1.0 < ATE ≤ 5.0	—
Symbol	Skull and crossbones	Skull and crossbones	Skull and crossbones	Exclamation mark	No symbol
Signal word	Danger	Danger	Danger	Warning	Warning
Hazard statement					
Oral	Fatal if swallowed	Fatal if swallowed	Toxic if swallowed	Harmful if swallowed	May be harmful if swallowed
Dermal	Fatal if brought into contact with skin	Fatal if brought into contact with skin	Toxic if brought into contact with skin	Harmful if brought into contact with skin	May be harmful if brought into contact with skin
Inhalation	Fatal if inhaled	Fatal if inhaled	Toxic if inhaled	Harmful if inhaled	May be harmful if inhaled





**Fig. 3** Short-term (acute) aquatic hazard for L(E)C50 for fish (96 h), crustaceans (48 h), and algae or other aquatic plants (72 h/96 h).

### Biodegradability concepts and definition

Organic chemicals are present in society's daily life and different mineral processing steps.<sup>28</sup> Thus, the environmental assessment of the biological transformation of these compounds proves to be extremely important.<sup>28</sup> Biodegradability is linked to the capacity of microorganisms to decompose or consume a determined substance, transforming it into energy, CO<sub>2</sub>, and water, and consequently, culminating in their own growth. In other words, biodegradation is the process of chemical breakdown of a substance caused by enzymes present in organisms.<sup>29</sup>

If a chemical degrades readily, it is improbable to bioaccumulate in the environment and therefore reach toxic levels, except if the chemical is highly toxic in low concentrations, the environmental exposure is high, or when its biodegradation products would be harmful.<sup>28</sup> Nonylphenol ethoxylates (NPEs), for instance, when biodegraded, are broken into nonylphenol (NP) and the ethoxylate chain. NP is ten times more toxic than the ethoxylate precursor, as it is an endocrine disruptor and carcinogenic.<sup>30</sup>

When developing new chemicals, it is desirable to be able to predict right from the beginning if the new material will rapidly degrade or be stable in the environment or treatment plants, and also how its biodegradation products behave.<sup>31</sup> Many compounds (such as determined synthetic polymers) are persistent in the environment, causing harmful effects on organisms and disrupting ecosystems. Therefore, methods to evaluate the biodegradability of compounds and UVCB's (unknown or variable composition, complex reaction products or biological materials) were developed and standardized. The biodegradability of single compounds in mixtures and in defined environments can be predicted through standard biodegradation tests, which are intended to simulate natural conditions to a certain degree. The most important system is the Organisation for Economic Cooperation and Development (OECD).<sup>32</sup> The OECD-test system has been incorporated into legislation by many European countries, including the registration, evaluation, authorization, and restriction of chemicals, REACH, and it is also widely accepted outside Europe. The OECD tests usually form the basis for regulatory measures and were created as a three-tier system of tests.<sup>32</sup>

The first is the "readily biodegradable" classification, by which a substance can be considered if it has reached a sufficient biodegradation in one of the OECD 301, OECD 310 (2014) or OECD 306 (1992) tests (REACH guidance R.7b, ECHA (European Chemicals Agency) 2017b).<sup>32</sup> One of the pass levels is 60% for the BOD (biochemical oxygen demand) or CO<sub>2</sub> pro-

duction compared to a measured or calculated reference value, which must be reached within 10 days after the beginning of the degradation. The maximum test duration is limited to 28 days.<sup>32</sup> The ratio of microorganisms to carbon amount must be relatively low; thus, the test conditions are very strict, conservative, and unfavorable compared to natural conditions, resulting in many chemicals not fulfilling these criteria even if they can be fairly biodegraded in the environment.<sup>32</sup>

The inherent biodegradability tests are less stringent and have a higher degrading power (*i.e.*, they favor biodegradation). This is due to the more favorable ratio of microorganisms to test substance carbon. Chemicals considered biodegradable in an "inherent test" are usually biodegraded under numerous natural and technical conditions, thus being classified as non-persistent if some specific criteria are met (*e.g.*, lag phase <3d, pass-level reached within 7 days (OECD 302 B-1992) or 14 days (OECD 302 C-1981)). Biodegradation above 20% and below the pass level of 70% might be evidence of primary biodegradability, indicating that stable degradation products are expected to be formed (ECHA 2017a).<sup>32</sup> On the other hand, the lack of biodegradation (<20%) in this test may be evidence that the test substance is persistent without the requirement for further testing.<sup>32</sup>

Simulation tests are the most predictive tools in the system, because they can simulate environmental conditions (fresh-water bodies of water and sediment, marine surface water, and anaerobic situations).<sup>32</sup> Besides OECD tests, several other standardized biodegradation tests, by ISO or CEN, can be considered (some of them included in the REACH test method regulation or in OECD guidelines). It often happens that new methods are developed within the ISO system, which are later adopted by the OECD and implemented in REACH, demonstrating high conformity between ISO and OECD tests.<sup>32</sup>

Although OECD guidelines constitute the primary international reference framework for biodegradability and ecotoxicity testing, their regulatory status differs across jurisdictions.<sup>33</sup> The EU formally embeds OECD methods within REACH, whereas the United States (TSCA), China (MEE), Australia (AICIS), and other regions apply nationally adapted systems that are largely harmonized with, but not legally bound to, OECD protocols.<sup>34</sup> As a result, biodegradability data generated under OECD guidelines are generally transferable across regulatory regimes, although local validation, additional endpoints, or country-specific procedural requirements may apply.

**Biodegradability prediction.** Microorganisms in general have the capacity to adapt themselves to a variety of ecosystems and environmental conditions, and they can degrade and metabolize a surprising range of organic compounds. They are susceptible to genotypic modification and enzymic re-orientation in response to environmental changes or carbonaceous substrate availability.<sup>35</sup> Many natural compounds persist and do not degrade under certain environmental conditions, such as the absence of water (water activity), osmotic effects, and extremes of temperature, among others. On the other hand, some chemicals are inherently non-degradable.<sup>35</sup>

A general or simple principle for estimating the biodegradation of industrial chemicals may be how different



chemicals are from natural products.<sup>28</sup> In this context, proteins, oils, and polysaccharides (carbohydrates) may be important structures to be studied as a basis for reagents. They are formed by smaller molecules, such as amino acids, fatty acids, and monosaccharides, which play an essential role in life in general as structural compounds, cell messengers, hormones, electron carriers, pigments, energy storage, and production.<sup>36</sup> These building blocks are functional for flotation, and there is still a world of possibilities to be explored. Three cycles that an organism undergoes to break down amino acids, fatty acids, and monosaccharides are amino acid oxidation, fatty acid catabolism, and glycolysis, respectively. It is understood that the more the compound fits into these metabolic routes, the easier it would be to biodegrade.

However, microorganisms can be flexible towards different substrates. For example, having linear chains (unbranched) in different surfactants allows organisms to degrade them effectively,<sup>37</sup> while recent studies showed that many branched surfactants are also readily biodegradable.<sup>38</sup> Additionally, there are biodegradability predictive mechanisms based on updated knowledge about various chemicals, derived from natural sources or petroleum. This knowledge can be used to predict or infer if a compound will be biodegradable, with a certain level of trust.<sup>39</sup> Therefore, the biodegradability prediction would be possible since microorganisms will more easily degrade compounds similar in structure to natural biomolecules. And from such a perspective, flotation reagents with structural similarity to natural building blocks may have higher chances of being eco-friendly chemicals.

**Biodegradability importance in flotation plants.** As flotation processes require about 50–85% (w/w) of water in the pulp, an alternative applied to make the process more environmentally friendly is recirculating internal water in the process and from tailings dams.<sup>40,41</sup> This is an effective method to reduce freshwater requirements and wastewater emissions in beneficiation processes.<sup>42</sup> However, the reused water may cause loss of selectivity/recovery in flotation in case the organic compounds only partially degrade or do not degrade effectively, lowering water quality parameters.<sup>40</sup> This is the primary reason why biodegradability is important, and it is also related to the safe discharge of effluent back into the environment without the need for advanced oxidative processes (for instance, Fenton and ozonation), thereby facilitating effluent treatment from both environmental and economic perspectives.<sup>43</sup> The main challenge related to biodegradability is that its behaviour is dependent on operational parameters in flotation circuits such as elevated ionic strength, high salinity<sup>44,45</sup> and presence of heavy metals.<sup>46</sup> Although OECD tests may indicate the nature of the substance or product and facilitate its selection, the complexity related to the specific system in which the product is being applied must be studied for each operation.

### Renewable feedstocks or biobased raw materials

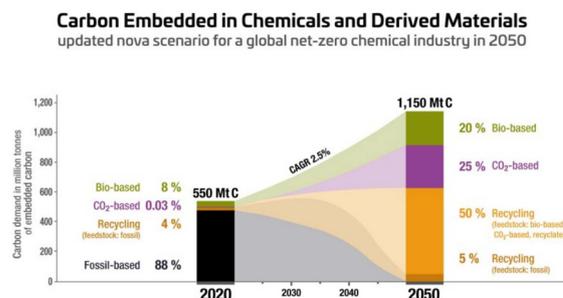
“A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable”.<sup>18</sup> Natural-based or biobased raw materials refer to pro-

ducts that consist of a substance (or substances) derived from living matter (biomass) and occur naturally.<sup>47</sup> The term ‘biomass’, according to the European Environment Agency (EEA), is defined as “the biodegradable fraction of products, waste and residues from agriculture (including vegetable and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste”.<sup>48</sup>

Biomass can be classified into primary products, and primary, secondary, and tertiary residues/side-streams.<sup>49</sup> Primary products are crops and other feedstocks cultivated for different purposes, with land use being a key element associated with them, and they are part of the debate over food *versus* other applications.<sup>49</sup> Fatty acids (such as those derived from soy, sunflower, and other crops) are linked to primary products from agriculture. Primary residues are materials that become available during harvest, remaining on the land and/or being collected for energy or other purposes, such as straw, treetops, and branches. Some agricultural primary residues were subjected to pyrolysis, transformed into oil, and applied to coal flotation, for example, partially substituting the main collector applied.<sup>50</sup>

Secondary residues become available during biomass processing, including oilseed meals, sawdust, black liquor, and bark. One example of a product from primary and secondary residues is lignin, which can be processed further for flotation applications.<sup>51</sup> Tertiary residues are generated after the consumption of food and other materials. Typical examples include organic waste, municipal solid waste, manure, demolition wood, and other post-consumer wood products. One example investigated was the application of frying oil in phosphate flotation.<sup>52</sup> Additionally, these are not directly linked to sustainability issues, but rather, more attention to circularity and recycling, as well as changes in consumption patterns, can influence their availability.<sup>49</sup>

One of the main challenges in using biomass is the competition for use, mostly focused on the energy sector, which results in limited availability for chemical production. In the long term, it is expected that fossil carbon sources will be replaced not only by biomass but also by CO<sub>2</sub> and plastics recycling, among others (Fig. 4).<sup>53</sup> Nowadays, around 13.1% of



**Fig. 4** Explorative scenario – carbon embedded in chemical products (2020/2050), reproduced from ref. 55 with permission from nova-Institute GmbH, copyright 2023.<sup>55</sup>



the raw materials used in the chemical industry are biobased (2021).<sup>54</sup> In this industry, the surfactant market typically utilizes more than 40% oil-based raw materials.<sup>54</sup> For such product groups, these have the advantage of providing a complex spectrum of functional groups by nature, which is directly and positively linked to the collector's production for flotation.

Approximately 30–50% of the examined and reported green flotation reagents explicitly focus on biobased materials. Biobased flotation reagents cover all categories of flotation chemicals, such as common depressants derived from starch (corn, potato, and wheat), widely used to depress iron oxides in reverse flotation, and carbonates in phosphate flotation. Cellulose derivatives, tannins, and lignin are naturally occurring compounds effectively used as depressants.<sup>56</sup> Modifiers, such as organic acids (*i.e.*, citric acid and humic acid, among others) from biomass sources, are used to adjust pulp conditions and mineral surface properties, acting as depressants and/or dispersants.<sup>57–59</sup> Collectors, such as fatty acids, are widely applied in the flotation of oxides, carbonates, and phosphate minerals. Biosurfactants, derived from microbial fermentation or plant extracts, have the potential to be applied as co-collectors for different mineral flotation processes.<sup>60–63</sup> Aminoacid- and peptide-based molecules also show potential for selective adsorption.<sup>64–66</sup> Frothers are less commonly studied but also have potential to increase research.

It was claimed that biobased materials naturally align with the criteria of being renewable, biodegradable, and eco-friendly. The primary reported benefits of biobased flotation reagents are that they offer environmental advantages, as they are biodegradable, but the concept that they offer lower ecological toxicity compared to conventional synthetic reagents is not always correct. They may reduce the potential environmental footprint and provide safer disposal methods. In terms of performance and effectiveness, biobased reagents may exhibit comparable or sometimes even superior performance compared to their synthetic counterparts, depending on the process and reagent system. They have potential for tailored specificity through chemical modifications of natural molecules. Biobased flotation reagents can be economically attractive due to lower production costs from raw materials (agricultural by-products, forestry residues, *etc.*). Their potential cost fluctuations are related to agricultural cycles or climate conditions. However, they have limitations such as variability in performance due to the heterogeneity of natural sources and stability concerns, as natural materials may degrade more rapidly or be affected by microbial activity. All these aspects must be considered when selecting raw materials and the physical–chemical properties of the developed product. Consequently, once the raw material is defined, the next step is to select/develop the process through which it will be transformed into the intermediate/final product.

### Green production

In green processes, preventing waste (P1) is one of the most important aspects towards a successful reaction, leading to the

avoidance of by-products and having a significant economic impact on production costs. Otherwise, most of the time, if waste or by-products are formed, they are usually discharged into the environment, consequently polluting it.<sup>67</sup> Continuous manufacturing (for example, represents an ally to the principle of prevention), reducing not only the time to market but also the number of synthetic steps, reagents, solvents, and power consumption, thereby decreasing the environmental footprint.<sup>68</sup> Besides waste prevention, the synthesis needs to be designed to incorporate the reagents into the final product as much as possible. This concept is known as “atom economy” (P2), as explained in eqn (1).<sup>69</sup>

$$\begin{aligned} \% \text{ Atom economy (AE)} \\ = \frac{\text{molar mass of atoms in the product}}{\text{molar mass of the reactants used}} \times 100 \end{aligned} \quad (1)$$

In organic synthesis, reactions of addition and rearrangement may be more atom-economical when compared to substitution and elimination reactions.<sup>67</sup> Thus, besides avoiding the use of hazardous reagents (P3), the generation of unsafe by-products could be involved in case the production controls fail.<sup>67</sup> Solvents should be innocuous to prevent unnecessary reactions (P5). As many solvents can be carcinogenic, water or green solvents should be applied. The design of bioproducts, using renewable carbon and converting it through clean processes, is key to the development of biobased solvents. For example, isoamyl acetate, isoamyl methyl carbonate, and ethyl isovalerate are all derived from fusel oil, a co-product generated by the ethanol industry.<sup>70</sup> Besides, it is ideal that the final product does not require purification or separation.<sup>67</sup>

As for chemical reactions, energy is often required and should be kept to a minimum necessary for the product to be formed (P6). Reactions carried out under mild conditions (0 °C to 70 °C) represent a green flag. A reaction run outside of this range, in an industrially acceptable range (–20 °C to 140 °C), gives a yellow flag, and over this range means a red flag for energy consumption.<sup>71</sup> Moreover, a suitable catalyst (P9) could be applied to reduce the amount of energy needed for the reaction, and to facilitate the transformation process, and sometimes be selective to specific reactions.<sup>67</sup> Derivatization (P8) (such as the application of blocking groups, protection, and deprotection) should be avoided since they add steps to the synthesis and ultimately form wastes.<sup>67</sup> In general, analytical methodologies for process control (P11) require further development to monitor and prevent the formation of hazardous substances effectively.

Finally, to avoid accidents (P12), volatile substances should be strongly circumvented.<sup>67</sup> This should be done, not only in the chemical processes, but also in final product formulations. Given that dangerous substances are often formed during physical or chemical transformations, green production is closely linked to designing processes with little or no toxicity, highlighting the importance of increasing knowledge in materials chemistry and life cycle analysis.<sup>72</sup> In the “benign design” concept, chemists and toxicologists must work



together to maximize the product's function while reducing toxicity and other physical hazards. This can be achieved by leveraging different aspects at the beginning of the development process.<sup>27</sup>

## Classification of the flotation reagents

As mentioned previously, for the reagent to be considered “green”, the four main pillars (biobased raw materials, green production, safer chemicals and biodegradability) must be considered and fit as much as possible, but mostly according to the following order and weights: (1) safer chemicals (40%), (2) biodegradability (30%), (3) biobased raw materials (20%), and (4) green process (10%) (Table 3). These weights were determined by applying the Analytic Hierarchy Process (AHP), a general theory of measurement.<sup>73</sup> This assessment considers that safer chemicals is the most important pillar, because safety is immediate and it is a non-negotiable value. Toxicity, ecotoxicity and physical risks posed by different chemicals can offer short-term and non-reversible risks to human health and the environment; therefore, they represent the most important criteria. The second criterion to determine if a flotation reagent is green would be biodegradability, as it affects the chemical after use, and contributes to long-term pollution control, it is directly linked to sustainability and long-term effects. In the case of a product presenting non-biodegradability, this can be circumvented *via* advanced oxidative processes, although this represents a higher economic expenditure. Biobased raw materials compound the third pillar and criterion, and it is linked to the control and origin of a chemical. It is important to ensure sustainability in the face of petroleum-derived raw materials, but it is also acknowledged that some safe chemicals can be derived from petroleum. The fourth pillar is the green process for producing these chemicals, which, with its lower impact, is also linked to long-term sustainability and operational efficiency. This is a concern mostly for the chemical industry than for the mining industry. Chemical processes can be made greener by applying renewable energy for heating, enhancing safety control in their complex processes involving harmful chemicals, and optimizing other parameters. In other words, these criteria and weights (Table 3) can be used to classify flotation reagent levels (Table 4): from level 1 (when the product fails to meet the minimum required sustainability parameters) to level 7 (when the product is made from biobased materials, produced *via* a green process, is non-toxic, and readily biodegradable, ideal for the circular economy with minimal environmental impact).

The proposed weighting scheme is based on the rationale mentioned, considering safety as the most important pillar, but it is also important to note that diverse operational or regional contexts may relocate the relative importance of the parameters. For instance, in countries with strict chemical regulations, the pillar “green process” could have a higher impact, while countries with low water availability could bear

**Table 3** Criteria and weights

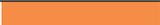
Criteria	Weight (%)
<b>Safer chemicals</b>	
Human (H)	0/15
Environment (E)	0/15
Physical hazards (PH)	0/10
<b>Biodegradability</b>	
No (N) – partial (P) – dangerous (D)/yes (Y)	0/30
<b>Biobased raw materials</b>	
0%	0
≤25%	5
>25% ≤ 50%	10
>50% ≤ 75%	15
>75 ≤ 100%	20
<b>Green process</b>	
0–3 criteria (N)	0
4–6 criteria (N)	5
7–9 criteria (Y)	10

higher impact for “biodegradability”. Although specific considerations for each country may slightly change the criteria and weights of this framework, it was considered a general approach to compare the chemicals from a “mining impact” perspective, considering what is more important for mining production regardless of the country it is based. In this regard, the framework could be homogeneously applied for different chemicals regardless of their application location.

## Application in flotation – are the reagents green?

Several flotation reagents are listed as “green” in various investigations. However, the four main pillars were not assessed for most of them,<sup>56</sup> and also for the main reagents applied nowadays. Thus, once the classification was determined, this study analyzed some of the main flotation reagents applied worldwide both west and eastern sides of the globe (depressants, collectors, and frothers) to establish their green profile (Table 5). Additionally, Table 6 was prepared to analyze the production of the reagents considered in Table 5. It is essential that researchers from the chemical industry and production companies discuss this information in depth, as their production methods may vary from one company to another.

**Table 4** Classification of the reagents based on the weights of the main pillars (biobased raw materials, green production, safer chemicals, and biodegradability)

Level	Classification	Description	Representation
1	Not green	Points: 0–29%	
2	Very low green	Points: 30–49%	
3	Low green	Points: 50–59%	
4	Moderately green	Points: 60–69%	
5	Green	Points: 70–79%	
6	Very green	Points: 80–89%	
7	Fully green	Points: 90–100%	



**Table 5** Analysis of the main reagents applied in flotation<sup>13,15,56,75,84,86,88,109,116,119–123,125–127,130,131,133–135,139,140,142,147–151,153,155,156,161–165</sup>

Reagent	Mineral	Biobased carbon [P7] (%)	Green production (Y/N)	Safer chemicals [P4] (Y/N)			Biodegradability [P10] (Y/P/D/N)	Classification (%)	Level
				H	E	PH			
Maize (corn) starch	Hematite, kaolinite	100 <sup>116</sup>	Y (9–9 principles) <sup>75</sup>	Y <sup>116</sup>	Y <sup>116</sup>	Y <sup>116</sup>	Y <sup>116</sup>	100	7
CMC	Carbonates, talc <sup>120</sup>	~65–90 <sup>121</sup>	N (3–9 principles)	Y <sup>119</sup>	Y <sup>119</sup>	Y <sup>119</sup>	Y <sup>120</sup>	85–90	6
Lignosulfonate	Carbonates (i.e., calcite), quartz, sulfides (i.e., pyrite) <sup>56</sup>	100	N (6–9 principles)	Y <sup>161</sup>	Y <sup>161</sup>	Y <sup>161</sup>	Y <sup>161</sup>	95	7
Sodium silicate	Silicates	0 <sup>84</sup>	N (5–9 principles)	Y <sup>125</sup>	Y <sup>125</sup>	Y <sup>125</sup>	N	45	2
Sodium cyanide	Gold, iron, and sulphides (pyrite, pyrrhotite, sphalerite, among others)	0 <sup>86</sup>	N (3–9 principles)	N <sup>126</sup>	N <sup>126</sup>	N <sup>126</sup>	D <sup>127</sup>	0	1
TOFA <sup>129</sup>	Apatite, calcite, dolomite, rare earth	100 <sup>130</sup>	N (6–9 principles) <sup>123</sup>	Y <sup>131</sup>	Y <sup>131</sup>	Y <sup>131</sup>	Y <sup>131</sup>	95	7
NPEO	Apatite, others <sup>133</sup>	0 <sup>88</sup>	N (5–9 principles)	N <sup>162</sup>	N <sup>162</sup>	N <sup>162</sup>	P <sup>134</sup>	5	1
Isotridecanol ethoxylate	Apatite, others	0	N (5–9 principles)	Y <sup>135</sup>	N <sup>135</sup>	N <sup>135</sup>	Y <sup>135</sup>	50	3
Isononyl ether-propylamine	Quartz and other silicates	0	N (4–9 principles)	Y <sup>163</sup>	N <sup>163</sup>	N <sup>163</sup>	Y <sup>139</sup>	50	3
Sodium ethylxanthate	Copper, lead, nickel, zinc, gold ores <sup>140</sup>	67	N (4–9 principles)	N <sup>142</sup>	N <sup>142</sup>	N <sup>142</sup>	D <sup>13</sup>	20	1
Sodium diisobutylidithiophosphate	Copper, molybdenum, zinc, and lead ores	0	N (5–9 principles)	Y <sup>147</sup>	Y <sup>147</sup>	N <sup>147</sup>	N <sup>147</sup>	35	2
NaDIBDTP									
Rhamnolipid <sup>164</sup>	Coal <sup>148</sup> , iron <sup>149</sup> , quartz <sup>164</sup>	100	Y (8–9 principles)	Y <sup>151</sup>	Y <sup>151</sup>	Y <sup>151</sup>	Y <sup>150</sup>	100	7
MIBC	Sulfides and oxides	0 <sup>109</sup>	N (6–9 principles)	Y <sup>15</sup>	Y <sup>15</sup>	Y <sup>15</sup>	Y <sup>153</sup>	65	4
Pine oil <sup>165</sup>	Sulfides and oxides	100 <sup>155</sup>	N (5–9 principles)	N <sup>156</sup>	N <sup>156</sup>	N <sup>156</sup>	Y <sup>156</sup>	55	3

## Depressants

Maize (corn) starch is usually applied as a depressant for hematite, kaolinite, and calcite. It is a biobased material, biodegradable, and non-toxic,<sup>116</sup> and it is a product obtained from a green process.<sup>117</sup> There are two main processes through which maize starch can be obtained.<sup>75</sup> The easier method is dry grinding of corn, which results in a different particle size distribution. The products would be sieved to separate the finest fraction (flour) from the coarse fraction (grit). Both fractions can be applied to flotation, and they also contain amounts of protein and oil, present in maize. Usually, the flour may be more effective, considering that gelatinization is better held when the granules are finer. The more sophisticated method is when starch extraction starts with the pulverization of the vegetable, followed by steeping in water to release the starch granules. Centrifugation or sieving is applied to the mixture to separate starch from fibers and proteins. The slurry is further washed and dried to obtain pure starch. The extraction maximizes yield and purity, directly impacting the quality and applicability of starch in various industrial applications.<sup>118</sup> Besides, corn stover can be applied for bioenergy and bioproducts through biochemical routes from different perspectives, including also waste prevention in the process.<sup>74</sup> Thus, based on the classification and assessments, maize starch produced only through grinding and sieving was classified as a completely green depressant (scores 100 from Table 5, and follows 9 principles from Table 6).

Carboxymethyl cellulose (CMC) is a biobased chemical, biodegradable and non-toxic,<sup>119</sup> applied as a depressant mostly

for carbonates and talc.<sup>120</sup> It is an anionic, water-soluble derivative of cellulose (depending on its degree of substitution (DS)), a linear polysaccharide composed of a glucose unit linked by  $\beta$ -1,4-glycosidic bonds.<sup>81</sup> CMC exhibits carboxymethyl groups ( $-\text{CH}_2\text{COOH}$ ) that replace the hydrogen atoms from some hydroxyl groups present in the cellulose infrastructure.<sup>76</sup> Its DS usually varies from 0.4 to 1.5, also impacting the amount (%) of biobased carbon present in the structure, mainly ranging from 65 to 90%.<sup>121</sup> The DS can be obtained through titration,<sup>122</sup> then allowing %C<sub>biobased</sub> to be calculated according to eqn (2).

$$\%C_{\text{biobased}} = \left[ \frac{N_{\text{carbonSbiobased}}}{N_{\text{carbonSbiobased}} + N_{\text{carbonSpetroleum based}} \cdot DS} \right] \times 100 \quad (2)$$

In this equation, the percentage of biobased carbon is calculated based on the cellulose backbone carbons (6 per glucose unit), that are renewable, and the number of carboxymethyl group carbons (2 per substitution), that come from fossil-derived reagents.<sup>76</sup>

In the CMC production process, a two-step reaction is applied involving first an alkalization process with NaOH in an organic solvent (such as isopropanol or ethanol) at a temperature of 30 °C and second, etherification using monochloroacetic acid (MCA) at 50 °C.<sup>77,79</sup> Moreover, side reactions may occur between the excess of NaOH and MCA, forming NaCl and sodium glycolate, interfering with the reaction yield.<sup>76,80</sup> MCA is a toxic substance, requiring extra safe handling.<sup>78</sup> Therefore,



Table 6 Green process analysis of some flotation reagents<sup>74–115</sup>

Reagents	Waste prev. [P1] (Y/N)	AE [P2] (Y/N)	Hazardous reagents [P3] (Y/N)	Solvents [P5] (Y/N)	High temperature [P6] (Y/N)	Catalyst [P9] (Y/NN <sup>a</sup> /N)	Derivatization [P8] (Y/N)	Green analyses [P11] (Y/N)	Volatiles [P12] (Y/N)	Number of principles
Maize (corn) starch	Y <sup>74</sup>	Y <sup>75</sup>	N <sup>75</sup>	N <sup>75</sup>	N <sup>75</sup>	NN <sup>75</sup>	N <sup>75</sup>	Y <sup>75</sup>	N <sup>75</sup>	9
CMC	N	N <sup>76</sup>	Y <sup>77,78</sup>	Y <sup>77</sup>	N <sup>79</sup>	NN <sup>80</sup>	Y <sup>80</sup>	Y	Y <sup>81</sup>	3
Lignosulfonate	Y <sup>82</sup>	Y	N <sup>82</sup>	N <sup>82</sup>	Y <sup>82</sup>	Y <sup>83</sup>	N	N	N	6
Sodium silicate	N <sup>84</sup>	Y <sup>84</sup>	Y <sup>85</sup>	N <sup>84</sup>	Y <sup>84</sup>	N <sup>84</sup>	N <sup>84</sup>	Y <sup>84</sup>	Y <sup>84</sup>	4
Sodium cyanide	N <sup>86</sup>	N <sup>86</sup>	Y <sup>86</sup>	N <sup>86</sup>	Y <sup>86</sup>	Y <sup>86</sup>	N <sup>86</sup>	Y <sup>86</sup>	Y <sup>86</sup>	3
TOFA	Y <sup>87</sup>	N <sup>87</sup>	Y <sup>87</sup>	N <sup>87</sup>	Y <sup>87</sup>	NN <sup>87</sup>	N <sup>87</sup>	Y	N <sup>87</sup>	6
NPEO	N <sup>88</sup>	Y <sup>89</sup>	Y <sup>90</sup>	N <sup>89</sup>	Y <sup>91</sup>	N <sup>89</sup>	N <sup>89</sup>	Y <sup>92</sup>	Y <sup>90</sup>	5
Isotridecanol ethoxylate	N <sup>93</sup>	Y <sup>93</sup>	Y <sup>90</sup>	N <sup>93</sup>	Y <sup>93</sup>	Y <sup>93</sup>	N <sup>93</sup>	Y <sup>94</sup>	Y <sup>90</sup>	5
Isononyl ether-propylamine	N <sup>95</sup>	Y <sup>95</sup>	Y <sup>96</sup>	N <sup>95</sup>	Y <sup>95</sup>	Y <sup>95</sup>	N <sup>95</sup>	N	Y <sup>96</sup>	4
Sodium ethylxanthate	N <sup>97</sup>	Y <sup>97</sup>	Y <sup>98</sup>	N <sup>97</sup>	Y <sup>99</sup>	NN <sup>97</sup>	N <sup>100</sup>	N <sup>101</sup>	Y <sup>98</sup>	4
Sodium diisobutylthiophosphate (NaDIBDTP)	Y <sup>102</sup>	Y <sup>102</sup>	Y <sup>103</sup>	N <sup>102</sup>	Y <sup>104</sup>	NN <sup>102</sup>	N <sup>102</sup>	N	Y <sup>103</sup>	5
Rhamnolipid <sup>105</sup>	Y <sup>106</sup>	Y <sup>106</sup>	N <sup>105</sup>	N <sup>105</sup>	N <sup>107</sup>	NN <sup>108</sup>	N <sup>105</sup>	N <sup>105</sup>	N	8
MIBC	N <sup>109</sup>	Y <sup>109</sup>	N <sup>109</sup>	N <sup>109</sup>	N <sup>109</sup>	Y <sup>109</sup>	N <sup>109</sup>	N	Y <sup>110</sup>	6
Pine oil	Y <sup>111</sup>	Y <sup>111</sup>	Y <sup>112</sup>	N <sup>113</sup>	Y <sup>114</sup>	Y	N <sup>111</sup>	N	Y <sup>115</sup>	5

<sup>a</sup> NN: not necessary for the process. Y, NN or N = green.

the process to obtain CMC can be considered not green (scores around 85% in Table 5 and follows 3 principles in Table 6). CMC production may be related to waste prevention, if alternative feedstocks and biomass residues are applied for the production; otherwise, the process usually creates waste that needs to be managed.

Lignosulfonates are products derived from lignin, the largest natural source of aromatic compounds coming from different biomass sources.<sup>123</sup> As lignin remains a largely unused fraction due to its recalcitrance and complex structure, there is an increasing amount of waste available for exploration.<sup>82</sup> Lignosulfonates are usually produced by sulfurous acid and/or a sulfite salt in the sulfite pulping process. In the lignosulfonate extraction step, wood chips are treated at high temperatures with aqueous sodium sulfite. The medium may be acidic, neutral, or alkaline. In a neutral process, sulfite liquor contains 15% Na<sub>2</sub>SO<sub>3</sub> and 1.5% Na<sub>2</sub>CO<sub>3</sub> mixed with wood chips at a 3 : 1 (liquid/wood, w/w) ratio and cooked at 175 °C for approximately 90 minutes. Anthraquinone has been used as a pulping catalyst in certain neutral sulphite processes.<sup>83</sup> The presence of sulfonated groups makes the product anionic and water-soluble.<sup>82</sup> Lignosulfonates can be applied as depressants on various minerals, such as carbonates (*i.e.*, calcite), quartz, and sulfides.<sup>56</sup> In flotation plants, the most used depressant of pyrite flotation, for instance, has been cyanide, despite its toxicity and environmental and health hazards.<sup>124</sup> In this regard, lignosulfonates have been studied as green pyrite depressants (scores 95% in Table 5 and follows 6 principles in Table 6) along with other organic polymers, thereby increasing the sustainability of the process.<sup>124</sup>

Sodium silicate is usually applied to depress a variety of silicates. It is produced continuously by reacting a silicon dioxide material with NaOH–Na<sub>2</sub>CO<sub>3</sub> solution,<sup>85</sup> at high temperature (240–275 °C) and pressure.<sup>84</sup> As this is an inorganic depressant, it is non-renewable and non-biodegradable. Although its production involves the use of basic chemicals and the generation of carbon dioxide, its concentration analysis is performed using its solid content, which is considered a green analysis. Although this chemical is considered relatively safe in its application, with low toxicity,<sup>125</sup> it was evaluated as 45% according to Table 5 and is produced according to 4 principles (Table 6).

Sodium cyanide (NaCN) is a corrosive material, toxic to humans and aquatic life.<sup>126</sup> It is inherently biodegradable, although most microorganisms do not survive in the presence of cyanide; some microorganisms can degrade it through a detoxifying mechanism.<sup>127</sup> NaCN is not a biobased material; its production is made through 2 main steps: (1) formation of hydrogen cyanide (HCN) through an Andrussow (platinum–rhodium catalyst) or Degussa (platinum catalyst) process, at extremely high temperatures;<sup>128</sup> (2) its crystals are produced by absorbing hydrogen cyanide gas in aqueous sodium hydroxide and then crystallizing the sodium cyanide solution that results from the absorption.<sup>86</sup> As this is a substitution reaction, it is not atom economical.<sup>86</sup> In the second step, temperatures may vary from 70 to 100 °C. The analytical procedure contained in



the patent is titration through silver nitrate, which is not considered a green analysis.<sup>86</sup> Its production is, therefore, not considered “green” (scores 0 in Table 5, with only 3 principles in Table 6).

### Collectors

TOFA is one of the most widely used fatty acids for mineral flotation worldwide, applied in apatite flotation in the US, Russia and South Africa, as well as monazite flotation in Australia, for instance.<sup>129</sup> It is produced by the distillation of crude tall oil, a renewable by-product from the paper and pulp industry originating from pine trees.<sup>130</sup> Tall oil is mostly produced from non-volatile fractions, fatty and rosin acid extractives, derived from the Kraft process (temperature varies from 150 °C to 180 °C), through acidulation of the fatty acid soap extracted at temperatures in the range of 105–108 °C.<sup>87</sup> Indirectly, this is already considered a high-temperature process.<sup>111</sup> Acid–base titration is commonly used to evaluate the products of a reaction, which can be considered a green analysis. TOFA is a safe chemical, non-toxic and biodegradable, 100% biobased and produced through a green process.<sup>131</sup> Since it scores 95 points from Table 5 and follows 6 principles from Table 6, it can be classified as a green collector.

Nonylphenol ethoxylate (NPEO) has been used as a co-collector in the flotation of different minerals, such as apatite.<sup>132,133</sup> It is a petroleum-derived product, produced from cyclic intermediates and crude coal tar *via* a 2-step reaction: the alkylation of phenol with mixed isomeric nonenes<sup>91</sup> (in the presence of an acid catalyst) to form the intermediate nonylphenol, followed by ethoxylation.<sup>88</sup> A strong base (such as KOH or NaOH) or a double metal cyanide (DMC) catalyst can be used for the ethoxylation process.<sup>89</sup> Ethylene oxide (EO) is the key reactant used in ethoxylation. EO is a toxic, extremely flammable gas.<sup>90</sup> This material is partially biodegradable, generating a bioaccumulative compound (NP).<sup>134</sup> Instead of applying NPEO, an alternative such as isotridecanol ethoxylate has been considered. The preparation process (hydroformylation) involves two steps: in the first, olefins react with a catalyst to form oligomers (C3)<sub>x</sub>, (C4)<sub>x</sub>, or their mixtures, at temperatures ranging from 100 °C to 300 °C; in the second step, the resulting saturated alcohol is ethoxylated.<sup>93</sup> The change in the carbon chain implies ready biodegradability,<sup>93</sup> safer chemicals related to human toxicity, and also a lower environmental impact.<sup>135</sup> Also, in ethoxylates, gas chromatography–mass spectrometry (GC–MS) can be used to detect and avoid the residual side reaction product 1,4-dioxane.<sup>94</sup> In general, NPEO cannot be classified as a green collector (Table 5: 5 and Table 6: 5 principles).

The isononylether propylamine has been used for silicate flotation, mainly quartz in reverse iron ore flotation.<sup>136,137</sup> Its production starts with isononanol, a product obtained from oil steam cracking and hydroformylation of hydrocarbons.<sup>138</sup> The alcohol reacts with acrylonitrile in the presence of an alkali metal hydroxide (cyanoethylation step) at a temperature of 45–70 °C, followed by hydrogenation using a catalyst with the temperature ranging from 50 to 250 °C.<sup>95</sup> This type of reac-

tion allows the formation of a final product that contains neither unreacted compounds nor by-products.<sup>95</sup> Either gas chromatography or cationic active titration can be used for analyzing product formation; however, neither is typically considered a green analysis method, although both can be improved and optimized. Acrylonitrile is a hazardous and volatile reagent, which increases the reaction process complexity. In the reactions considered, the atom economy is high with no formation of waste. Also, the considered etheramine exhibits some toxicity, but it biodegrades and does not remain in the environment.<sup>139</sup> As the specific compound mentioned is neither biobased nor follows green production in its synthesis process, it is considered a low green collector (Table 5: 50% and Table 6: 4 principles).

Xanthates started to be applied for flotation around 100 years ago, with the development of the building block chemical carbon disulfide.<sup>14</sup> The ethylxanthate is usually applied as the most selective flotation agent for sulfide ores, containing copper, lead, gold, nickel, and zinc.<sup>140</sup> It can be produced instantaneously by dissolving caustic sodium or potash in ethanol at a temperature of 50 °C, followed by cooling (15 °C) and finally reacting with carbon disulfide.<sup>97,100</sup> This reaction does not require high temperatures; however, producing the reagent carbon disulfide requires high temperatures of around 1000 °C, even with the application of a catalyst.<sup>99</sup> The analysis used to measure the concentration of xanthate produced is a titration, typically involving BaCl<sub>2</sub>, which makes the process non-green.<sup>101</sup> Carbon disulfide is a flammable and toxic compound that requires higher safety standards to be handled.<sup>98</sup> Although the product ethylxanthate is readily biodegradable, the decomposition of xanthate into CS<sub>2</sub> can be harmful to the human central nervous system with long-term exposure.<sup>141,142</sup> Thus, it receives a low score (20% from Table 5 and 4 principles from Table 6).

Sodium diisobutylthiophosphate (NaDIBDTP) has traditionally been used to concentrate different sulfidic ores.<sup>143</sup> It is obtained through a reaction between isobutanol, phosphorus pentasulfide (PPS), and a basic substance, such as sodium hydroxide.<sup>144,145</sup> Both alcohol and PPS are flammable substances, requiring careful handling, and PPS is also toxic to the aquatic environment.<sup>103,146</sup> NaDIBDTP is not readily biodegradable; it is corrosive but presents lower toxicity compared to the reagents used in its production.<sup>147</sup> Typically, the synthesis temperature ranges from 40 °C to 120 °C, and it does not require the use of solvents,<sup>102,145</sup> scoring 35% from Table 5 and following 5 principles from Table 6.

As an example of a green compound being studied for flotation, the rhamnolipid was also evaluated using this framework. This is a new biosurfactant being studied for different flotation processes, such as for coal<sup>148</sup> and iron.<sup>149</sup> This material is biodegradable,<sup>150</sup> non-toxic<sup>151</sup> and produced *via* biosynthesis, applying *Pseudomonas aeruginosa*, or other types of microorganisms such as *Burkholderia thailandensis* and *Escherichia coli*.<sup>108</sup> Although the production of secondary metabolites (antibiotics and proteases) may happen, they can also be controlled, increasing the yield of the process. The



biosynthesis happens around the temperature of 37 °C and at pH 7,<sup>107</sup> but it depends on the strain applied. The main carbon substrates applied can be glucose or glycerol<sup>107</sup> (including waste from biodiesel production),<sup>152</sup> but rhamnolipids can be produced from various types of low-cost substrates, such as carbohydrates, vegetable oils and even industrial wastes.<sup>106</sup> The production and separation of the final product may involve the use of solvents, but a solvent-free process has already been adopted by the industry.<sup>105</sup> This compound scores 100% in Table 5 and follows 8 principles in Table 6.

### Frothers

Frothers are applied to many different flotation processes, from sulfidic to non-sulfidic. The most applied frother is MIBC, which has low toxicity and is readily biodegradable.<sup>15,153</sup> MIBC is produced in three reaction steps: (1) the preparation of diacetone alcohol by the condensation of acetone; (2) the dehydration of diacetone alcohol into mesityl oxide; and (3) the hydrogenation of mesityl oxide into methyl isobutylketone, and then into the corresponding alcohol.<sup>109</sup> Acetone is a flammable reagent, as is the product MIBC, which alerts mining companies due to the explosion risk associated with its use.<sup>15,110</sup> MIBC production can be made greener if acetone is produced *via* a biotechnological route.<sup>154</sup> This scores 65% in Table 5 and follows 6 principles in Table 6.

Pine oil is another important frother applied in flotation, although its use diminished over the years.<sup>12</sup> It is a product obtained from different plant parts such as resin, woods, twigs, and cones, and also its composition and properties are governed by the raw material from which it is produced, the geographical location of trees, and the climatic conditions of growth.<sup>155</sup> Pine oil is inherently biodegradable and classified as flammable and toxic for human health.<sup>156</sup> Usually, the oleoresin, collected from a pine tree through tapping, contains 20% turpentine and 65% rosin.<sup>155</sup> The pine oleoresin is washed, and turpentine and water are distilled separately.<sup>113</sup> To synthesize pine oil, turpentine is hydrated *via* catalysis with a mineral acid, such as orthophosphoric acid, and in the end, pine oil is collected as an essential oil.<sup>113,114</sup> Since turpentine is considered a hazardous reagent for health and is also volatile, and pine oil has its own health and environmental hazards, the process is not considered green.<sup>112,115</sup> This compound scores 55% in Table 5 and follows 5 principles in Table 6. Although MIBC is not biobased, it gained a higher classification when compared to pine oil (Table 5: 65 *vs.* 55, respectively), according to this framework.

### Framework limitations

Although the framework is consistent and can be successfully applied to compare different chemicals, it was built bearing the mining company perspective in mind. As a result, chemical production, although more complex to analyse, becomes secondary in this evaluation. It means that an adjustment for the chemical industry would be necessary in terms of applicability in their own processes and detailed evaluation. The

framework does not account for differences in mineral processes, because it is based on the chemical nature of the applied products, regardless of the operation. Reagent blends can also be evaluated through this framework, considering the formulation proportions of each compound: it means that each substance added needs to be evaluated individually, and in the end, the proportion applied in the formula must be included for the final summation. Although, this is neither mentioned nor calculated because formulations are usually companies' property and therefore, confidential. Costs are not directly included in this framework, but it is understood that for a complete evaluation, costs related to process and wastewater treatment must be considered in the business evaluation.

## The path for development

In the past, the performance of the flotation reagents was the most important factor evaluated, not giving much consideration to the manufacturing process and other impacts they could cause.<sup>14</sup> Currently, numerous studies investigate various types of chemicals that may offer a more sustainable profile. This shows a tendency to look at other aspects that, before, were ignored or not considered important. Looking into the profile of the different chemicals applied for flotation, it is possible to understand that they are already coexisting in the flotation environment around the world (macrocosm), and coexisting in different formulations, as a microcosm (Fig. 5). To change the whole, the starting point is the microcosm (product and formula), but with the comprehension of the macrocosm. This is part of the components inside the chemical industry, which serves the needs of the mining industry (which must be viewed on a higher scale: both producer and user countries, as well as globally).

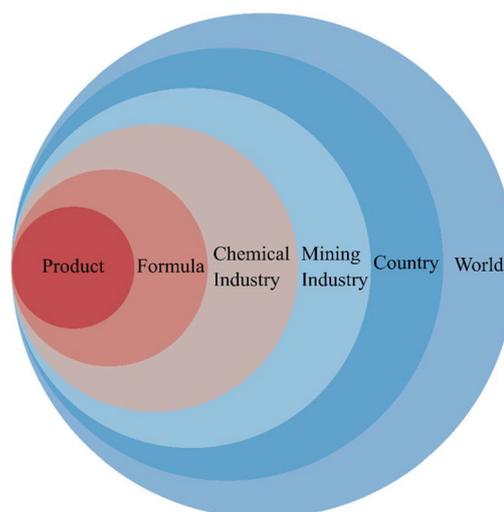


Fig. 5 From the microcosm to the macrocosm.



The microcosm/macrocosm is a nested system. In this type of complex system, “each system is enclosed by, and is enclosing, other systems”.<sup>157</sup> This means that what happens at the level of a molecule or formulation propagates outward through regulations, markets and supply chains until it has spread globally with consequences. The microcosm can be defined by molecular structure, purity, toxicity and ecotoxicity, biodegradability, synthesis characteristics (such as energy and water intensity), feedstock origin, required dosage and performance efficiency. All these properties are concentrated in a local system, but they determine how the product interacts with enclosing systems. The macrocosm (formed by industries and countries around the world) is compounded by human health, different environmental systems, governance and regulatory regimes, industrial value chains, global trade and resource flows. Regulatory systems are usually the transition layer between the microcosm and macrocosm. Through the necessary data: physicochemical properties, toxicological and ecotoxicological endpoints, persistence and bioaccumulation, substances will be classified, restricted or phased out based on data evidence. The outcomes at the macroscale can be represented by market access or exclusion, regional bans or global conventions and incentives for safer alternative application. A molecular design choice can shift a substance from “high concern” to “acceptable”, altering its global regulatory footprint. The next enclosing system, the industries, act as amplifiers, which means that industrial adoption scales microcosm decisions.<sup>158</sup> Engineers and chemists can choose the reagent class and modulate process conditions (pH and temperature, among others). In the macrocosm, these choices affect safety requirements, waste treatment infrastructure, emission profiles, corporate Environmental, Social and Governance (ESG) performance and license to operate in different regions. Mining industries will adopt formulations that meet performance needs, minimize regulatory risk, reduce operational complexity and align with sustainability reporting requirements. A reagent that requires lower dosage and generates biodegradable residues can reduce transport volumes, hazardous waste handling and compliance costs across multiple countries, which makes global adoption economically viable.

Supply chains transform local formulation choices into planet-scale flows. Companies with strong power in the supply chain have the advantage of resources, information and control, providing not only competitive advantage, but also the fulfillment of environmental responsibility.<sup>158</sup> Decisions made in the microcosm regarding raw material sourcing, the number of steps in a synthesis process, the use of critical or geographically concentrated inputs and energy intensity per kg of product may have consequences in the macrocosm regarding the carbon footprint of global logistics, vulnerability to geopolitical disruptions, environmental burden shifting between regions and social impacts in upstream extraction zones.<sup>159</sup> Changing a formulation for effective use may focus on abundant, non-critical feedstocks and regionally available raw materials to increase resilience and reduce global environmental and social risks.

Local reagent choices directly support UN Sustainable Development Goals (SDGs).<sup>160</sup> From the microcosm to the macrocosm, local choices affect, respectively, (a) from lower toxicity chemistry to reduced global health and ecosystem burden; (b) from biodegradable structures to less accumulation across ecosystems; (c) from renewable feedstocks to decoupling growth from fossil carbon; and (d) from process-efficient reagents to lower global energy and water use. Sustainability means what is used and also how much and how often. Small efficiency gains at the microcosm level multiply across millions of tonnes globally.

Microcosm defines the rules while macrocosm defines the consequences. A product or formulation is a unit of decision. Regulation, industry and supply chains are systems of propagation, and sustainability emerges when microcosm design aligns with macrocosm constraints. In this sense, green reagents and responsible formulation design are not only local optimizations between chemical and mining industry labs, but global interventions executed at the molecular scale.

## Conclusions

In this work, a definition and conceptual framework for green flotation reagents were established to improve the understanding of the chemicals most commonly used and tested in flotation. A classification system was also proposed to guide the development of future reagents with improved sustainability profiles for different flotation processes. It is recognized that enhancing the sustainability of reagents should be achieved progressively, based on a thorough understanding of the chemical market, production routes, and key properties such as physical hazards, human and environmental toxicity, and biodegradability.

To support practical decision-making, different weights were assigned to the four pillars of green flotation reagents: 40% safer chemicals, 30% biodegradability, 20% biobased raw materials, and 10% green process. On this basis, a priority ranking approach for green reagent R&D can be derived, in which candidate molecules or formulations are first evaluated according to their weakest-performing pillar. Reagents that are technically critical but score poorly in the “safer chemicals” and “biodegradability” pillars, such as sodium cyanide, highly toxic amines, xanthates, or flammable frothers, should be considered top priorities for substitution or molecular redesign. Compounds with acceptable toxicological profiles but fossil origin or energy-intensive synthesis may be ranked at a secondary level, targeting improvements in raw material sourcing and production routes.

While improvements in the “green process” pillar largely depend on the chemical industry (*e.g.*, renewable energy use, catalyst replacement, and cleaner synthesis), the remaining pillars have a more direct and immediate impact on mining operations. Because multiple reagents coexist in flotation circuits, the framework highlights urgent actions focused on reducing acute and chronic hazards, flammability, and



environmental persistence. Each component of a formulation should therefore be systematically screened, and modifications that lower toxicity or remove unnecessary hazards should be implemented wherever technically feasible, while maintaining or improving metallurgical performance.

The framework also enables differentiated green transition pathways for mining companies of different scales. Large mining companies, with greater R&D and investment capacity, can act as early adopters by co-developing and piloting novel green collectors, depressants, and frothers, including bio-based or biotechnology-derived alternatives, and by integrating life-cycle assessment into reagent selection. Small and medium-sized enterprises, in contrast, may initially focus on short-term, low-risk measures, such as replacing the most hazardous or regulated chemicals with commercially available alternatives that already show improved safety and biodegradability, and progressively upgrading their reagent portfolios in line with the proposed ranking.

The case of NPEO illustrates this stepwise transition. Although NPEO has long been used for apatite flotation and is still applied in some developing countries, it has been banned in Europe. Its replacement with isotridecanol ethoxylates represents an intermediate improvement in the environmental profile, even though these alternatives remain petroleum-derived. According to the present classification, such substitutions constitute a first step, while further progress would involve evaluating bio-based or low-toxicity surfactants with comparable performance.

Finally, natural and biotechnological products, such as bio-surfactants, offer promising long-term options, although their competing uses in food, health, and cosmetics must be considered. Overall, the proposed four-pillar framework, combined with a priority ranking logic and scale-dependent transition strategies, provides a practical tool to guide both reagent R&D and industrial implementation, enabling a gradual and technically feasible shift toward greener flotation systems.

## Conflicts of interest

There are no conflicts to declare.

## Note added after first publication

This version replaces the Advance Article published on 05/03/2026, which did not include the final revisions. The Royal Society of Chemistry apologises for any confusion.

## Data availability

This study was carried out using publicly available data from the different sources cited in this work. As this is a theoretical article, there is no supplementary information to be shared or reported.

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