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Review

Active Treatment of Contaminants of Emerging Concern in Cold Mine Water Using Advanced Oxidation and Membrane-Related Processes: A Review

Sébastien Ryskie [1], **Carmen M. Neculita** [1,2,*], **Eric Rosa** [1,3], **Lucie Coudert** [1,4] and **Patrice Couture** [5]

[1] Research Institute on Mines and Environment (RIME), Université du Québec en Abitibi-Témiscamingue (UQAT), Rouyn-Noranda, QC J9X 5E4, Canada; Sebastien.Ryskie@UQAT.ca (S.R.); Eric.Rosa@uqat.ca (E.R.); Lucie.Coudert@uqat.ca (L.C.)

[2] Canada Research Chair in Treatment of Contaminated Mine Water, RIME, UQAT, Rouyn-Noranda, QC J9X 5E4, Canada

[3] Groupe de Recherche sur l'Eau Souterraine (GRES, Groundwater Research Group), RIME, UQAT, Amos, QC J9T 2L8, Canada

[4] Canada Research Chair in Repurposing of Mine Waste, RIME, UQAT, Rouyn-Noranda, QC J9X 5E4, Canada

[5] Centre Eau Terre Environnement, Institut National de la Recherche Scientifique (INRS), Québec, QC G1K 9A9, Canada; Patrice.Couture@ete.inrs.ca

* Correspondence: Carmen-Mihaela.Neculita@uqat.ca

Abstract: Responsible use and effective treatment of mine water are prerequisites of sustainable mining. The behavior of contaminants in mine water evolves in relation to the metastable characteristics of some species, changes related to the mine life cycle, and mixing processes at various scales. In cold climates, water treatment requires adaptation to site-specific conditions, including high flow rates, salinity, low temperatures, remoteness, and sensitivity of receiving waterbodies. Contaminants of emerging concern (CECs) represent a newer issue in mine water treatment. This paper reviews recent research on the challenges and opportunities related to CECs in mine water treatment, with a focus on advanced oxidation and membrane-based processes on mine sites operating in cold climates. Finally, the paper identifies research needs in mine water treatment.

## 1. Introduction: Contaminants of Emerging Concern (CECs) in Mine Water

Sustainable mining implies a balance between economic profitability, safety, social acceptability, and environmental protection [1]. Given these factors, issues related to the mitigation of mining impacts on water resources inevitably arise. Optimizing low-cost water treatment approaches is critical to ensuring sustainable mining. This goal represents a major challenge as the global demand for mineral resources intensifies and diversifies [2], while the legislation regulating mining activities constantly evolves [3]. An integrated use of hydrological, geochemical, and isotopic tools in mining operations is also evolving [4]. Contaminants of emerging concern (CECs) are a central issue in this contemporary mining context.

In municipal and industrial wastewater, CECs include a wide range of highly soluble, persistent, and potentially toxic substances. Generally, there is limited knowledge about their concentrations (mostly because of poor knowledge on their quantification methods) and detrimental impacts [5]. These contaminants originate from natural or anthropic sources. Improved knowledge on the sources, transport, and spatiotemporal variability of CECs is an ongoing research need, especially for mixed-use watersheds, for better understanding of associated risks, and developing monitoring and mitigation strategies [6].

In mining, throughout history, new or emerging contaminants evolved with metallurgy challenges, scientific knowledge, and regulations [7,8]. As a result, new or CECs

in mine water have specific features. They are not necessarily new chemicals and may have been present for a long time, but their presence or significance are only now being recognized, often because of increasing exploitation of low-grade ores, such as As from refractory gold mining [9]. The data about their characterization and toxicity are often scarce, the methods of detection are nonexistent or at an early stage, and there is no international definition of a new or emerging contaminant [10]. The CECs in mine water could even be contaminants that have already been treated but suddenly need to be mitigated to a new order of magnitude (especially in sensitive environments, such as cold climate (e.g., geographical isolation, extreme cold, strong winds, and erosion, salinity from de-icing agents or other, freeze-thaw cycles)). The definition of a CEC could also change geographically or for a different activity sector.

A review of Canadian legislation related to new contaminants or CECs in mine water and the development of treatment processes in the 1980s, 1990s, 2000s, and 2010s identified the following defining characteristics in each decade: (1) Before the 1980s, base metal mines were required to control metal concentrations in their effluents, but gold mines were not regulated [11]. Field-testing of cyanide destruction systems was reported (INCO or SO_2/air process discovery), followed by the testing, patenting, and implementing of all kinds of hydrogen peroxide-based processes. By the end of the 1980s, various types of water treatment systems were constructed and operated to control pH and treat dissolved metals, cyanides (and derivatives), total suspended solids, and so on. (2) In the 1990s, SO_2/air process was deployed at large scale. Acute aquatic toxicity was reportable but not regulated. There was a lot of research to lower copper and ammonia concentrations, but not much implementation of the findings. The 1990s also saw the first attempts to use metal precipitants. (3) In the 2000s, the International Cyanide Management Code (ICMC) and similar regulations meant that cyanide destruction now targeted the mill tailing pipe, not only final discharge, and the Metal Mining Effluent Regulations (MMER) meant that discharge water must not be acutely toxic. The decade also witnessed improved ammonia treatment as well as increased thiocyanates (SCN^-) biochemical treatment, and growing research on toxicity sources. (4) In the 2010s, the review of MMER saw the discussion and addition of new water targets, i.e., Metal and Diamond Mining Effluent Regulations (MDMER). Although Se was not mentioned, other parameters were tightened or introduced under MMER. Some mines in northern regions started to work on desalination projects and were required to meet the Canadian Council of Ministers of the Environment (CCME) criteria at mine site closure. In some countries, mining permits involved respecting sulfate parameters; and zero liquid discharge (ZLD) and zero liquid waste (ZLW) were introduced. The evolution of regulations in Canada's (MMER) and Quebec's (Directive 019) mining industry is presented in Figure 1.
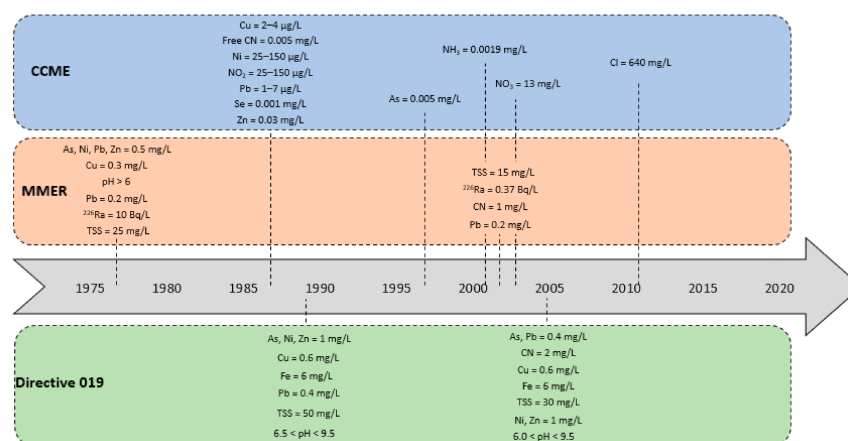
Figure 1. Regulation evolution for the mining industry in Canada [11–14]. CCME: Canadian Council of Ministers of the Environment; Metal Mining Effluent Regulations: MMER; TSS: Total Suspended Solids.

Therefore, the current basic classification of CECs in mine water includes new contaminants (e.g., rare earth elements (REE), radioactive elements, Se, Mn); contaminants of emerging interest (e.g., salinity, sulfate), for which environmental contamination issues were not fully comprehended earlier; and "well-documented" contaminants (e.g., As, thiosalts, N-based compounds, xanthates, SCN^-), for which new issues (e.g., persistent aquatic toxicity) recently emerged, particularly in cold climates (at low temperature and high salinity) [7,8,15]. By their very nature, CECs are of growing concern for the mining industry. The definitions of some CECs based on scientific knowledge of different substances in mine water are presented in Figure 2.
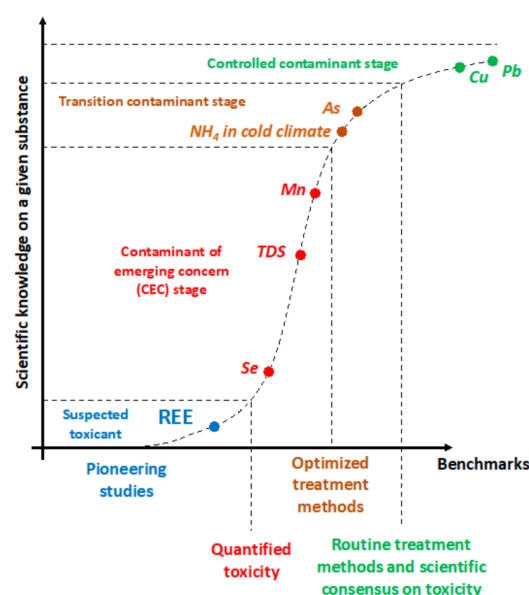
Figure 2. Contaminants of emerging concern (CECs) definitions based on scientific knowledge of different substances in mine water. REE: Rare Earth Elements; TDS: Total Dissolved Solids.

Based on the context outlined above, this paper provides an overview of the efficiency of selected processes and materials for the treatment of CECs from mine water. Background concentrations of selected CECs (As, Se, Mn, salinity, thiosalts, NH_3-N, and REE) in natural water are proposed as a basis for comparison with mine water. The treatment processes focus on As and Se, thiosalts, xanthates, N-based compounds (cyanides, NH_3-N, and SCN^-), and salinity. Regarding REE treatment, several comprehensive reviews are available, including two recent articles on the challenges and opportunities of their treatment and potential recovery from mine water [16–18]; thus, these elements will be not discussed in this review, even though they are of emerging concern. This review focuses on mine sites in cold climates to identify some priority issues related to the treatment of CECs. Questions relating to the treatment of CECs are of particular interest because of (1) the potential toxicity of these substances and (2) the gaps in the scientific knowledge required to define criteria for the discharge of mine water into the environment. The present study aims to contribute to the scientific efforts required to overcome this problem.

2. Characteristics of CECs

2.1. Background Concentrations of CECs

In this paper, As, Se, and Mn are considered as leading inorganic elements, given their importance as mine-related CECs and their known impacts on human health and the environment. In addition, xanthates, salinity, thiosalts, and nitrogen compounds were selected mainly because their ecotoxicological and cumulative effects remain uncertain even at low concentrations, especially with mixed contamination [7–9].

The geogenic sources of As include several minerals (e.g., arsenides, sulfides, oxides, arsenates, arsenites) that can be concentrated in mineralized areas [19]. In rocks, As

typically ranges between 0.5 and 2.5 mg/kg [20], for an average crustal abundance of 1.5 mg/kg [21]. Common sources of As are As-bearing sulfides, which are often abundant in areas exploited for base metals, silver, and gold. In natural water, As mainly occurs as oxyanions of arsenite (As(III)) or arsenate (As(V)), while As-bearing organic species are generally less abundant [19]. In a review of worldwide data from large rivers, dissolved As concentrations of 0.11 to 2.71 µg/L, for a world average of 0.62 µg/L, were reported [22]. In groundwater, As concentrations can vary widely, with reported concentrations from <0.05 µg/L to 79.0 µg/L, based on 813 samples from European aquifers [23]. In acid mine drainage, As concentrations up to 12 g/L (pH < 1.8) and Fe up to 20 g/L, in Carnoulès abandoned mine site, France [24], or droplets of liquid on the arsenolite (As_2O_3) crust with extreme high As concentrations ($80-130$ g/L, pH close to 0), have been reported [25].

Se concentrations in rocks are generally low, and the average crustal abundance is 0.05 mg/kg [21]. Se can be enriched in phosphate rocks (up to 300 mg/kg), coal (1–20 mg/kg), and black shales (up to 600 mg/kg) [21,26]. In natural water, Se mainly occurs as selenite (Se(IV)) and selenate (Se(VI)) [21]. In European surface water, reported Se concentrations range from <0.01 µg/L to 15.0 µg/L, for a median value of 0.340 µg/L [27], while, in European groundwater, Se ranges from <0.015 to 247 µg/L, for a median value of 0.50 µg/L [23]. Se concentrations of 1.5 to 33 mg/L were reported in mine water [28].

Mn is the third most abundant transition metal on earth. The average concentrations found in natural water are 0.004 to 2 µg/L [7]. Mn is found in seven oxidation states in nature (0, 2+, 3+, 4+, 5+, 6+, and 7+), but the most common forms in water are Mn^{2+}, Mn^{3+}, and Mn^{4+}. Mine drainage, whether acidic or neutral, often contains a high concentration of Mn, which can have an undesirable impact on ecosystems. In mine water, Mn concentrations range from 0.02 to 352 mg/L, depending on the location and type of mineralogy [7]. Studies demonstrate that Mn can have effects on aquatic organisms, but they are little known, and the impact of Mn on aquatic toxicity remains to be clarified to better guide the selection of treatment methods [7].

Xanthates are the most used collectors in the flotation of sulfurous minerals, and they can be found in mine tailings in concentrations sufficient to have a toxic effect on aquatic fauna [29]. More than 11,000 metric tons of xanthates are consumed annually worldwide in the form of sodium isopropylxanthate (40%), sodium ethylxanthate (30%), sodium isobutylxanthate (15%), and potassium isopentylxanthate (10%) [30]. These molecules act as collectors by rendering the surfaces of the mineral particles hydrophobic and, thus, help them to cling to air bubbles during the flotation process [31]. Xanthates can be toxic to aquatic organisms such as *Daphnia magna* at concentrations of 0.1 to 1 mg/L [31,32]. The concentrations in mine water can vary depending on the type of ore processed. In general, 300 to 500 g of xanthates per tonne of ore is required to obtain satisfactory separation [33]. Residual concentrations ranging from 0.2 to 9 mg/L have been reported in process water [34]. Xanthates can also increase the bioaccumulation of metals by forming hydrophobic complexes with metals such as Zn, Cd, Pb, and Cu. These complexes facilitate the assimilation of metals by organisms through cell membranes [33]. The toxicity of xanthates is mainly linked to their degradation path, which causes the formation of carbon disulfide, which is volatile and slightly soluble in water. The xanthates have a half-life varying between 2 and 8 days, depending on the length of the alkyl chain, for a temperature of 15 °C. However, degradation in cold climates has not yet been studied [33].

Mine water salinity is an integrative parameter, which is characterized by the cumulative concentration of the most common ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, CO_3^{2-}, and SO_4^{2-}) [35]. Salinity, electrical conductivity (EC), and total dissolved solids (TDS) are correlated. TDS may include an inorganic fraction (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, CO_3^{2-}, and SO_4^{2-}) and an organic fraction (dissolved organic carbon—DOC) [36]. In mine water, TDS and salinity consist mainly of inorganic ions. The EC, which is defined by water's ability to allow the transport of electric charge, is an indication of the degree of water mineralization, providing information on dissolved elements (in ionic form) [37]. The high concentration of TDS results in an increase in the salinity of mine water. Salinity

persists after the treatment of the mine water, which often even increases it. Moreover, salinity can have a detrimental impact on the aquatic toxicity depending on the species present in water and their concentrations. For example, the concentration of Ca^{2+} or water hardness can reduce the toxicity of Cl^- and SO_4^{2-} [38]. Once dissolved solids that form salinity are transported into the environment, they are likely to cause toxicity [39].

Thiosalts are metastable sulfur oxyanions, naturally present in concentrations ranging from very low to a few hundred mg/L, such as in highly acidic crater-lake water [40]. Thiosalts are the common intermediate species of sulfur oxidation in metal sulfides (e.g., pyrite, pyrrhotite), in the presence of sulfur-oxidizing bacteria [41,42]. The main thiosalts species are thiosulfate ($S_2O_3^{2-}$), trithionate ($S_3O_6^{2-}$), and tetrathionate ($S_4O_6^{2-}$), with $S_2O_3^{2-}$ being the dominant thiosalt species [43,44]. In mine water, thiosalts are mainly generated (up to 60%) during the milling and flotation of sulfide ores, and at high pH (9.4–10.7) and alkalinity [45]. Other factors that contribute to the acceleration of thiosalt formation include the following: sulfides content of ores (5 times more thiosalts generated in ores with 80 to 90% sulfides vs. 25 to 30% sulfides); residence time during flotation (proportional); temperature (double amount at 40 °C vs. 25 °C); agitation rate in flotation (accelerated oxidation kinetics); and grinding operation (significant reduction of thiosalts generation (86%) during grinding at pH 10.7 in a solution deaerated with nitrogen gas) [46]. A recent study evaluated the effect of freeze/thaw cycles on thiosalts concentrations using column tests with tailings mainly dominated by pyrrhotite and serpentine [47]. Results showed that $S_2O_3^{2-}$ could top up to 10 g/L for columns subjected to freeze/thaw cycles relative to 7.2 g/L for those at an ambient temperature. Additionally, $S_4O_6^{2-}$ reached concentrations of 2.6 g/L in freeze/thaw columns and 2.2 g/L in the ambient columns. Another study showed the increased reactivity of minerals during freeze/thaw cycles [48], thus, supporting previous observations [47].

Nitrogen compounds, including NH_3-N, NO_2^-, and NO_3^-, are naturally present in the environment, usually at low concentrations. Human activity tends to add more nitrogen compounds in natural streams. In the presence of phosphorus, the eutrophication of stagnant or low-flow water sources can often occur, even in cold climates [49]. In the mining industry, the two major sources of nitrogen compounds are explosives and cyanides. Nitrogen-based blasting agents (e.g., ANFO—ammonium nitrate fuel oil) are used in mining to extract the commodities from their ore bodies. The explosives that are not completely degraded in the explosion can be dissolved in the water and then pumped at the surface during the dewatering process [50]. In addition to explosives, which are common to all types of mines, in the gold and silver extraction process, cyanides are also needed for their efficient recovery (>90%, at 71 mg Au/t) [51].

Cyanidation, which was deemed a major advance at the end of the 19th century, remains the most efficient and least expensive separation process for gold and silver extraction, even though cyanides are toxic and nonselective, and generate effluents that are highly complex to treat [52,53]. The main issue related to these effluents is their mixed contamination with several groups of undesirable substances (e.g., cyanides and their derivatives, such as NH_3-N and SCN^-, metals), which requires multiple treatment steps for the final effluents to respect the physicochemical and toxicity discharge criteria. Two contaminants closely related to aquatic toxicity, even though not regulated by the Canadian law, are NH_3-N and SCN^- [52]. While the major source of NH_3-N (i.e. cyanides) is specific to gold mining, a nitrogen source associated with explosives (ANFO) is common to all mine effluents. The efficient treatment of NH_3-N and SCN^- requires their oxidation to bicarbonate and nitrate, in addition to sulfate (for SCN^-). The high flow rates of mine effluents, together with the very slow kinetics of NH_3-N oxidation, especially at low temperatures, supports the need for new, robust, adapted, and low-cost processes with low or no temperature and pH dependence [50], in addition to limited residual salinity creation.

Cyanides require treatment before wastewater is discharged into natural streams and can lead to the formation of NH_3-N [52]. If sulfur is present in the processed ores (as sulfide minerals and partially oxidized sulfur intermediates), toxic derivatives (SCN^-) can also

be formed at high pH and alkalinity [51]. Even though SCN^- is less toxic than CN^-, its higher stability makes it more complex and difficult to treat [52].

The compilation of different contaminants, including their typical concentration in natural and mining environments, sources, and treatment methods is presented in Table 1. The schematic representation of the CECs evolution in the mining environment is presented in Figure 3.

Table 1. Compilation of different contaminants, including their typical concentration, source, and treatment methods.

Contaminant	Natural Environment Concentration (µg/L)	Mining Environment Concentration (mg/L)	Possible Source of Contamination	Applicable Processing Methods	References
Mn	0.004–2	0.02–352	Acid and neutral mine drainage	Co-precipitation Sorption Ion exchange Membrane filtration Oxidation and precipitation Biological	[7,54]
Se	<0.01–15	1.5–33	Mine drainage	Membrane filtration Ion exchange Evaporation Co-precipitation Electrocoagulation Photoreduction Adsorption Biological	[27,28,55,56]
Xanthates	N/A	0.2–9	Flotation process	Advanced oxidation processes Natural degradation	[34,57]
Thiosalts	N/A	<700	Acid mine drainage and mineral processing	Advanced oxidation processes Lime neutralization Biological Natural degradation Electrochemical oxidation Membrane filtration	[43,45,58]
Salinity (TDS)	<1000	<16,000	Mine drainage	Thermal processes Coagulation-flocculation Membrane filtration Aerobic treatment	[15,59,60]
SO_4^{2-}	3000–30,000	100–5000	Mine drainage	High density sludge treatment ChemSulphide process Biopaq – Bioteq Sulfatogenic bioreactor Passive treatment Sorption Dispersed alkaline substrates Membrane filtration	[15,61]
As	0.11–2.71	<130,000	Mine drainage and hydrometallurgical processes	Co-precipitation Membrane filtration	[9,25]

Table 1. *Cont*.

Contaminant	Natural Environment Concentration (µg/L)	Mining Environment Concentration (mg/L)	Possible Source of Contamination	Applicable Processing Methods	References
NH_3-N	<1000	46	Explosives and cyanide treatment	High pH stripping Membrane filtration Nitrification-denitrification Natural degradation Anammox Electro-oxidation Electrocoagulation Adsorption Advanced oxidation processes	[50,62–64]
NO_2^-	<1600	4.4	Explosives Biological treatment	Denitrification Membrane filtration Advanced oxidation processes	[50,64,65]
NO_3^-	<10,000	25–100	Explosives Cyanide treatment Biological treatment	Denitrification Membrane filtration	[50,65,66]
CNO^-	N/A	28	Cyanide treatment	Natural degradation Ozone Biological	[64,67]
SCN^-	N/A	168–680	Cyanide treatment	Ozone Electrochemical oxidation Biological treatment Ferrates Advanced oxidation processes	[52,64]

N/A: Not Applicable; TDS: Total Dissolved Solids.
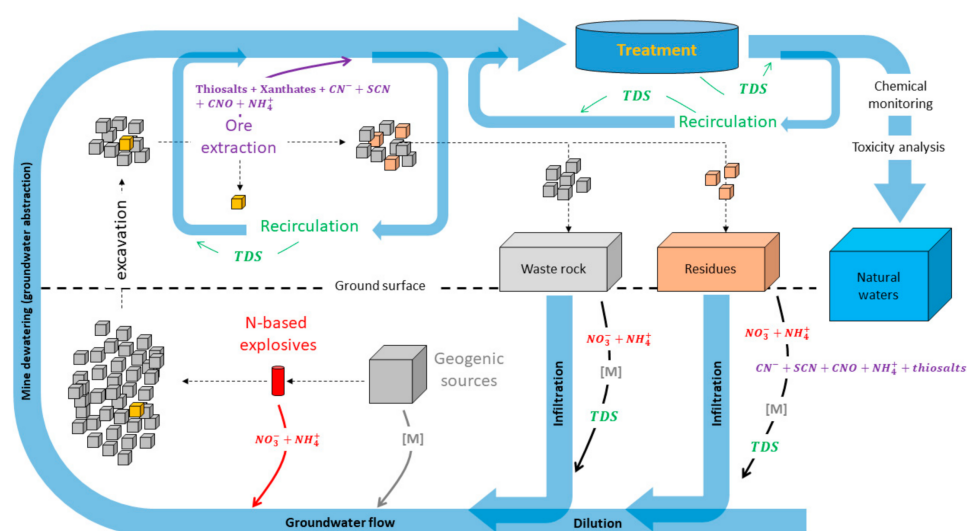
Figure 3. Schematic representation of the CECs evolution in the mining environment. [M]: metal or metalloid; TDS: Total Dissolved Solids.

2.2. Persistent Aquatic Toxicity

The aquatic toxicity of mine water is an important parameter to consider during mining operations. As an example of cold climate, the Canadian context is discussed. At the provincial level in Quebec, operating mining companies must comply with the guidelines set out in Directive 019 [68]. In Canada, at the federal level, they must comply

with the Metal and Diamond Mining Effluent Regulations (MDMER) [14]. In addition to maximum authorized concentrations of several contaminants in mine water, the MDMER stipulates that the acute toxicity testing on rainbow trout (*Oncorhynchus mykiss*) and water fleas (*Daphnia magna*) must be performed once a month. Because *D. magna* is generally more sensitive to acutely lethal environments than rainbow trout, research often relies on *D. magna* as a representative indicator for acute toxicity. Even though *D. magna* is used widely in regulatory assessment, *D. pulex* is commonly found in Canadian lakes, streams, and rivers—that is, in almost all eutrophic and permanent watercourses [69]. Comparative evaluation of the acute toxicity for *D. magna* and *D. pulex* of sulfate-rich neutral mine water from active gold mines showed a greater sensitivity of *D. pulex* compared to *D. magna*, before and after the treatment by electrocoagulation, in toxicity tests using standard reconstituted hard or natural dilution water [70].

Water from mining activities tends to be highly charged with contaminants such as metal(loid)s, salinity, nitrogen compounds, and, in some cases, xanthates. Aquatic toxicity of some CECs (e.g., xanthates, thiosalts) in mine water is incompletely assessed and under-documented, as opposed to others (e.g., As, Se) for which the literature is abundant. A compilation of lethal (LC50) and effective (EC50) concentrations of the different contaminants for *D. magna* is presented in Table 2.

Several studies have demonstrated the impact of these various contaminants on aquatic fauna. Although mining companies are governed by standards for aquatic toxicity, even when the acute toxicity criteria for regulated species (*D. magna* and rainbow trout) are met, the entire wildlife food chain can be affected by chronic effects [71,72]. Depending on the contaminant speciation and water mixes, bioavailability and synergistic or competitive effects in their fixation on binding sites on a biotic ligand might occur [71].

Table 2. Lethal (LC50) and effective (EC50) concentrations of CECs reported for *Daphnia magna*.

Contaminant	LC50 (mg/L)	EC50 (mg/L)	Test duration (h)	Hardness (mg CaCO$_3$/L)	Temperature (°C)	pH	References
Mn	N/A	9.3 10.27	48	45 240	21	6.5–8.5	[73]
Se	N/A	0.71	48	72	21	6.5–8.5	[73]
Na-ethyl xanthate Na-isopropyl xanthate Na-isobutyl xanthate K-amyl xanthate K-pentyl xanthate	N/A	0.35 3.7 3.6 3.67 3.0	N/A	N/A	15	N/A	[33]
$S_2O_3^{2-}$ $S_4O_6^{2-}$	N/A	300 750	N/A	N/A	N/A	N/A	[45]
Ca^{2+}	N/A	52 560	48	45 240	21	6.5–8.5	[73]
Cl^-	2600	N/A	24	N/A	N/A	N/A	[74]
Na^+	N/A	1640 423.13	48	45 240	21	6.5–8.5	[73]
K^+	N/A	93 160.45	48	45 240	21	6.5–8.5	[73]
SO_4^{2-}	7000	N/A	48	N/A	N/A	N/A	[74]
As	N/A	2.4 7.4 74	48	72 45 240	21	6.5–8.5	[73]
Cu	0.004 0.012	N/A N/A	48 48	44 ± 4 150 ± 10	N/A N/A	N/A	[75]
Zn	0.82 0.1 0.655 0.3 1.29	N/A N/A N/A N/A N/A	48 24 24 48 48	N/A 45 196 44 ± 4 150 ± 10	N/A N/A N/A N/A N/A	N/A	[69] [76] [76] [75] [75]

Table 2. *Cont.*

Contaminant	LC50 (mg/L)	EC50 (mg/L)	Test duration (h)	Hardness (mg CaCO$_3$/L)	Temperature (°C)	pH	References
NH$_3$-N	1.980	N/A	24	N/A	20	7	[77]
NO$_3^-$	2047	N/A	48	156–172	N/A	N/A	[78]
N-NO$_2^-$	N/A	23	48	N/A	20	N/A	[79]
CNO$^-$	18	N/A	48	N/A	N/A	N/A	[80]
SCN$^-$	57.4	11.3	48	N/A	N/A	N/A	[52]
	0.63–32	N/A	96	75	8–16		

N/A: Not Applicable.

To reduce the dispersion of contaminants in the environment and prevent the deterioration of aquatic fauna, the federal government has introduced regulations. The MDMER requires that all metal mines produce an effluent that is nontoxic for rainbow trout and *D. magna*, in accordance with Environment and Climate Change Canada's methods of analysis. If there is mortality for more than 50% of the organisms in 100% of the whole effluent concentration during a period of 48 h for *D. magna* or 96 h for rainbow trout, the sample is considered as having failed the toxicity test [14]. If the lethality test is failed, the mining company must investigate the causes of toxicity.

The most common approach to determining the causes of toxicity is the Toxicity Reduction Evaluation (TRE) method. A step-by-step protocol was developed to help identify and confirm the causes and sources of toxicity and to eliminate them [58]. The first step of this protocol, known as Toxicity Identification Evaluation (TIE), is to identify the contaminant(s) responsible for the toxicity. Once the identification has been carried out, the next step is Source Identification (SI). The final step, Toxicity Treatability Evaluation (TTE), is to evaluate possible treatments or modify water management approaches to eliminate toxicity. During this process, it is important to have optimal communication and coordination between the various stakeholders, such as operators, toxicologists, chemists, and the engineering team, so that the TRE is a success [58].

Studies on the direct and indirect toxicity of thiosalts do not show a correlation between concentration and mortality of the species regulated by provincial and federal laws for acute and sublethal toxicity tests. In general, it is agreed that thiosalts are not directly acutely toxic at concentrations commonly found in mining effluents but rather indirectly due to the generation of latent acidity, which causes a decrease in pH [43]. Concentrations up to 4.1 g/L of S$_2$O$_3^{2-}$ did not entail acute toxicity to rainbow trout [45]. However, toxicity occurred when the pH of the water dropped to below 5. Direct toxicity test results consistently showed that sublethal toxicity, sublethal toxicity to *C. dubia* was high but total thiosalts concentrations were low, and vice versa [45]. The same report found that S$_2$O$_3^{2-}$ is more toxic to all organisms (96 h LC50 for *C. dubia* = 59 mg/L; 96 h LC50 for *L. minor* = 498 mg/L; 96 h LC50 for *P. promelas* = 665 mg/L) than S$_4$O$_6^{2-}$ (96 h LC50 for *C. dubia* = 562 mg/L; 96 h LC50 for *L. minor* > 901 mg/L; 96 h LC50 for *P. promelas* > 891 mg/L), which results in a non-additive toxicity of the polythionates, thus, explaining the absence of correlation between total thiosalts and toxicity [45]. The IC25 values for indirect toxicity are low (high toxicity) for all organisms when the pH drops below 5, except for *L. minor* (IC25 > 100% at pH 3.1; no toxicity) [45]. Confirmed toxicity at circumneutral pH indicates that other contaminants such as Cu and Se may add to thiosalts toxicity [45]. Further research on thiosalts toxicity is required considering the extreme concentrations recently reported [47] and the increased reactivity of minerals (and, therefore, leaching of other contaminants) during freeze/thaw cycles [48], especially for mines operating in cold climates. These studies should focus on the cooperative toxic effect with other metals and non-additive toxicity of polythionates.

Mixed contamination of mining effluents can entail complexities because of the interactions between the contaminants. The thermodynamic equilibrium between the mineral and chemical phases determines the speciation of the contaminants. These reactions are dependent on the temperature and the balance of the mineral, gas, and aqueous phases. Bacterial activities can also have a role as a biocatalyst for the various reactions that occur [81].

Several models of aquatic toxicity prediction that consider the mixture of different contaminants as well as the physiology of biota already exist. These models determine the speciation of inorganic elements according to the physicochemical parameters of water and then determine the LC50 values. For example, the Biotic Ligand Model (BLM) can be used for this type of prediction [82–84]. Mixed contamination can significantly contribute to aquatic toxicity. One of the most widely used bioassays in the world for acute aquatic toxicity is that of *D. magna*, one of the most sensitive crustaceans [85]. Examples of *D. magna* toxicity in the mining industry are presented in Table 3. Mixed contamination can sometimes have pronounced effects on *D. magna*. The combination of various contaminants according to different physicochemical properties modifies speciation, bioavailability, and equilibrium concentrations in the final effluent. For example, the hardness of water, a parameter that has a significant effect on the toxicity of metals, reduces the bioavailability of these metals and, therefore, increases the toxic concentration [83]. At high concentrations, the hardness can have an opposite effect by increasing osmotic stress in biota [86]. Calcium can also have a protective effect on *D. magna* by reducing the absorption of metals such as Ni, Zn, Se, and Cd [83,86].

Another study has shown that water with very high hardness and alkalinity and containing high concentrations of Ca^{2+}, Mg^{2+}, CO_3^{2-}, and HCO_3^- can have a toxic effect on *D. magna*. A calcite shell ($CaCO_3$) forms over its entire surface and causes its disintegration following its death (LC50, 72 h). In this case, the head disintegrated first [87].

Table 3. Examples of *D. magna* toxicity in mine water.

Location	Exploitation Type	Parameters	*D. magna* Toxicity (Toxic Units—TU)	References
South Korea	Metal plating plant final effluent	pH = 7.58 DOC = 131.1 mg/L Hardness = 46 mg $CaCO_3$/L Cu dissolved = 0.36 mg/L Cl^- = 12,841 mg/L Br^- = 2307 mg/L	6.5	[88]
	After treatment by ion exchange	Cl^- = 2840 mg/L	<1	
South Korea	Final effluent of acid rock drainage treatment plant before pH correction	pH = 4.51 DO = 4.11 mg/L DOC = 3.87 mg/L Hardness = 2408 mg $CaCO_3$/L Al dissolved = 31.87 mg/L Cu dissolved $\leq$ DL Fe dissolved = 13.92 mg/L Zn dissolved = 1.39 mg/L	5.66	[88]
	After pH correction	pH = 7.0 Al dissolved = 0.093 mg/L Cu dissolved = 0.001 Fe dissolved = 0.011 mg/L Zn dissolved = 0.05 mg/L	<1	
South Korea	Mixed effluents of electronics plant	pH = 8.55 DOC = 139.5 mg/L Hardness = 178.8 mg $CaCO_3$/L Cu total = 1.5624 mg/L Cu dissolved = 0.4793 mg/L	35.46	[88]

Table 3. *Cont.*

Location	Exploitation Type	Parameters	*D. magna* Toxicity (Toxic Units—TU)	References
Canada (QC)	Final effluent, LaRonde mine, Agnico Eagle (04-03-1999 to 20-02-2001)	pH = 7.8–9.2 CN total = 0.005–0.36 mg/L CNO^- = 3.9–231 mg/L SCN^- = 73–293 mg/L NH_3-N = 20–88 mg/L SO_4^{2-} = 1350–2370 mg/L DOC = 35–93.6 mg/L Ca = 470–670 mg/L Cu = 0.02–0.14 mg/L Zn $\leq$ 0.01–0.26 mg/L	1–50.5	[89]
Canada (QC)	Final effluent, LaRonde mine, as reported by SGS Lakefield (06-05-2001)	pH = 8.05 TDS = 3320 mg/L CN total = 0.05 mg/L CNO^- = 21 mg/L SCN^- = 57 mg/L NH_3-N = 32.6 mg/L NO_2-N = 2.78 mg/L NO_3-N = 22 mg/L SO_4^{2-} = 2200 mg/L DOC = 12.4 mg/L Ca = 713 mg/L Cu = 0.016 mg/L Cu dissolved = 0.011 mg/L Na = 177 mg/L Zn = 0.02 mg/L Zn dissolved $\leq$ 0.01 mg/L Conductivity = 2710 μmhos/cm Hardness = 1820 mg $CaCO_3$/L DO = 9.4 mg/L	1.68	[89]
South Korea (Daeduck, Damyang county)	Mine drainage	pH = 6.1 Hardness = 16 mg $CaCO_3$/L Zn = 0.156 mg/L Pb = 0.0402 mg/L Cu $\leq$ DL Cd = 0.0013 mg/L	1.6	[75]
South Korea (Myungbong, Boseong county)	Mine drainage	pH = 7.8 Hardness = 50 mg $CaCO_3$/L Zn = 4.797 mg/L Pb = 0.0015 mg/L Cu = 0.0296 mg/L Cd = 0.0176 mg/L	22.9	[75]

DL: Detection Limit; DOC: Dissolved Organic Carbon; DO: Dissolved Oxygen; TDS: Total Dissolved Solids; TU: Toxicity units.

One way to predict the aquatic toxicity of mixed contamination is to sum the toxic units (TU). The TU is equal to the concentration of a contaminant in the water divided by the LC50. If the sum of the TUs of all the contaminants in the mixture is greater than 1, the water is considered toxic to the organism in reference. The validity of this principle was confirmed with real effluents, but the LC50 were corrected in relation to water hardness [75]. Considering the reduction in toxicity in response to an increase in hardness, formulas can be used to correct the LC50. Although this method predicts aquatic toxicity with a confidence rate of up to 89% in some cases, a high iron concentration can be an inhibiting factor in the estimation of toxicity because of amorphous iron precipitates [90]. A high DOC concentration can also have an important role in the complexation of metals and decreases the confidence rate of the prediction of aquatic toxicity by this method [88].

3. Treatment of CECs in Mine Water

Treatment strategies usually begin by identifying the problem, followed by setting objectives, and considering potential solutions based on constraints related to Best Available Technology Economically Achievable (BATEA), specific regulatory criteria, environmental impacts (residual contamination and aquatic toxicity), social acceptability, and license to operate [91,92]. The review of available literature showed that at least three main priorities can be identified in responsible management of mine water in cold climates: (1) development of sustainable treatment processes with limited energy consumption; (2) control of the residual salinity, after treatment; and (3) safe handling of produced sludge, after the recovery of potential economical elements or the immobilization of undesired ones. Contrary to temperate climates, the characteristics of cold climates contribute to additional challenges and opportunities in mine water treatment. The technologies presented in this paper can be used in cold climates with good treatment performance as the cold temperature has less impact on their treatability mechanisms compared to conventional treatments.

3.1. Advanced Oxidation Processes (AOPs)

Some AOPs fit into these requirements as they are efficient at low temperatures and allow for the complete oxidation of several contaminants in water using environmentally friendly oxidants, based on the hydroxyl radical, such as peroxone (H_2O_2+O_3) [93], Fenton-like (H_2O_2 and Fe^{3+} catalyst) [94,95], ferrates (Fe(VI)) [96], and O_3 microbubbles [63,64,97] or persulfate-based AOPs [98]. The peroxone was found more effective in the degradation of naphthenic acids and toxicity reduction than ozonation (at high doses), a costly treatment for oil sands process-affected water [99]. However, peroxone proved inefficient or inhibitory for NH_3-N treatment in a synthetic effluent [64].

In a recent study, the use of H_2O_2 to remove thiosalts from a synthetic and real mine effluent at 8 °C and 22 °C showed that a long reaction time was required for optimal efficiency [100]. The important role of temperature on the removal of thiosalts was confirmed. In fact, results showed that low temperatures enhance the stability of polythionates, but also seem to partially oxidize $S_2O_3^{2-}$ in the presence of H_2O_2 as oxidizing agent. At higher temperatures, 96% thiosalts removal from a real effluent was reached, but the oxidation of intermediate S species was incomplete and reaction time was 7 days.

The Fenton process consists of H_2O_2 activation with basically an iron catalyst to generate a hydroxyl radical, a powerful and nonselective, environmentally friendly oxidant. The Fenton-like process was found highly efficient (>99% of 1 g/L SCN^-) and a potential economical option for SCN^- partial oxidation (at pH 2.5–3) into cyanides to be returned to the leaching of gold and silver from their ores [94]. Consistently, at 21 °C, Fenton-like gave 84% and 22% of SCN^- and NH_3-N removal (at initial concentrations of 1 g/L and 40 mg/L, respectively), whereas at 4 °C the efficiency of SCN^- degradation decreased to 73% [95]. This AOP has major advantages, as the iron catalyst is easily available; the process is environmentally friendly and entails low residual toxicity and operating costs [101].

Electrochemical AOPs have been gaining popularity for limiting As toxicity, through oxidation of As(III) to As(V), and its subsequent removal. Electrochemical treatment methods have the advantage of using electrons as a reagent, thus, reducing the amount of added chemicals and residual salinity [102]. Bio-electrochemical AOPs have also received growing interest for organic CECs treatment in municipal wastewater because of the reduced cost of electricity. In fact, electro-Fenton (EF) and bio-electro-Fenton (bio-EF) are the eco-friendliest and most cost-efficient processes for the treatment of recalcitrant contaminants compared to other electrochemical methods [102,103]. In bio-EF, electrons are generated through microbial activity at the anode, and H_2O_2 is in situ generated at the cathode. H_2O_2 is then available to react with an iron catalyst to form hydroxyl radicals, as in the conventional Fenton process. In a study on EF in a dual chamber microbial fuel cell, results showed that As(III) removal efficiency was of 94% at optimal oxidation current efficiency. However, the removal process was incomplete for As(V) [103], and the final concentration did not meet the criteria specified by federal law [14].

Most publications focus on EF/bio-EF efficiency for the degradation of organic contaminants. Very little information is available on their performance for oxidation and removal of micropollutants, despite a promising application to the mining industry. Therefore, forthcoming research should focus on assessing EF and bio-EF performance on removal of oxidizable CECs in synthetic and especially real mine water, including As, NH_3-N, and thiosalts [104].

New research reported the satisfactory efficiency of ferrates for NH_3-N and SCN^- removal from highly contaminated mine effluents, but not simultaneously [105]. The wet Fe(VI) efficiency was evaluated on three synthetic and two real gold mine effluents contaminated by SCN^- and/or NH_3-N. Results showed that Fe(VI) oxidized more than 97% of SCN^-, while the NH_3-N increased up to 50%, after SCN^- oxidation in the presence of NH_3-N, within 1 h. A second step of NH_3-N treatment would, thus, be warranted. The main concerns, especially with wet Fe(VI) use, are the high pH and dissolved solids content of treated water (when high doses are required), that can adversely affect water quality downstream of discharge and its toxicity [96,106]. However, as the Fe(III) salt source for wet Fe(VI) production could be nitrates, chlorides, or sulfates, the residual contamination could vary: (1) from a four-time increase of residual nitrates with $Fe(NO_3)_3$, to (2) high residual chlorides with $FeCl_3$ and the oxidant used in the Fe(III) to Fe(VI) oxidation (sodium hypochlorite, NaClO), and (3) to no increase of residual sulfates with $Fe_2(SO_4)_3$ [106].

3.2. Ozone Microbubbles

The efficiency of several AOPs (O_3 microbubbles, UV, and H_2O_2) was also tested for NH_3-N removal from several synthetic (70 mg/L NH_3-N) and five actual mine effluents [64]. The tests started in batch mode, for optimizing the performance, followed by in continuous flow with one real effluent. Results showed that O_3 microbubbles gave the best efficiency. Indeed, more than 92.6% of the initial NH_3-N was treated, at pH 9, within 90 min. The use of Br^- as a catalyst increased treatment efficiency, whereas the combination of UV with O_3 was less efficient than O_3 alone under the conditions tested. Moreover, the presence of cyanides, cyanate, SCN^-, and metals adversely influenced NH_3-N removal efficiency, which ranged from 27.8 to 99.3%. Polishing final steps were required for the removal of the coloration that developed in some treated mine effluents. These results were consistent with previous findings on O_3 microbubbles that showed NH_3-N complete removal in a synthetic effluent (100 mg/L), at pH 9, in about 7.2 ks, whereas at pH 6 only 20 mg/L of NH_3-N were removed [63]. Moreover, they are consistent with reported findings on the oxidation of As(III) (50–200 µg/L) to As(V), at pH 7, within less than 25 min in a synthetic effluent [107]. The O_3 microbubbles process showed also satisfactory efficiency in thiosalts removal (99%) from a synthetic effluent [100]. The use of O_3 microbubbles for NH_3-N treatment in mine water has distinctive advantages, including the fast kinetics of the process, complete oxidation of several contaminants in mixing effluents, and no residual salinity creation in the treated water. Recently, the ultrasounds combined with ozonation and SrO-Al_2O_3 as a catalyst showed to be promising for NH_3-N treatment [108]. With a combination of ultrasounds at a frequency of 25 kHz vs. 270 W ultrasonic power and ozone, the NH_3-N conversion and N_2 gas yield were 83.2% and 51.8%, respectively.

The mode of diffusion of O_3 in water is an important process, allowing mass transfer to the gas-liquid interface. Indeed, due to the low solubility of O_3 in water, the injection method can increase the process efficiency, for example, by using microbubbles [109]. The microbubbles have a diameter of 10 to 50 µm, and a very high gas-liquid interfacial contact surface, then a very low ascent rate. The phenomenon that makes the use of microbubbles attractive for water treatment is the reduction in their size until their implosion in the liquid phase, unlike the coarse bubbles that always rise to the surface [109]. Two major advantages characterize microbubbles. First, there is higher ozone solubilization with higher internal pressure, forcing greater mass exchange at the gas-liquid interface. Ozone then forms hydroxyl radicals depending on the physicochemical properties of water. Second, microbubbles implosion phenomenon also generates hydroxyl radicals [109].

The use of AOPs such as ozone, microbubbles, and sonochemical cavitation in the mining sector is very rare. In recent years, these processes were also adapted for use with mine effluents, with satisfactory results. Comparative performance of ozone, microbubbles, peroxone (mixture of ozone and hydrogen peroxide), and sonochemical cavitation for mine water at different scales are presented in Table 4.

Table 4. Treatment performance of ozone, microbubbles, and ultrasound on mine water or compounds used in flotation processes.

Treatment Type	Industry	Influent	Effluent	Scale	References
Ozone microbubbles followed by coagulation-flocculation	Gold mine underground water	pH = 6.7 Eh = 445 mV T = 22 °C NH_3-N = 22 mg/L NO_2^- = 5.5 mg/L NO_3^- = 185 mg/L Cu = 0.154 mg/L Fe = 1.06 mg/L Mn = 3.41 mg/L Zn = 9.6 mg/L	pH = 8.7 Eh = 410 mV T = 22 °C NH_3-N = 0.78 mg/L $NO_2^- \leq$ DL NO_3^- = 180 mg/L Cu = 0.01 mg/L Fe = 0.16 mg/L Mn = 0.58 mg/L Zn = 0.2 mg/L	Pilot in continuous flow	[64]
Ozone microbubbles	Gold mine process water after cyanide destruction	pH = 9 Eh = 295 mV T = 22 °C NH_3-N = 34.6 mg/L NO_2^- = 6 mg/L NO_3^- = 48 mg/L CNO^- = 15.8 mg/L SCN^- = 135 mg/L Total CN = 0.04 mg/L Cu = 1.52 mg/L Fe = 0.5 mg/L Mn = 0.3 mg/L Zn = 0.29 mg/L	pH = 9.3 Eh = 382 mV T = 36 °C NH_3-N = 5.4 mg/L $NO_2^- \leq$ DL NO_3^- = 151 mg/L CNO^- = 12.5 mg/L $SCN^- \leq$ DL Total CN = 0.05 mg/L $Cu \leq$ DL $Fe \leq$ DL Mn = 0.06 mg/L $Zn \leq$ DL	Pilot in batch mode	[64]
$O_3 + H_2O_2$	Gold mine process water	CN = 172.5 mg/L pH = 11 Turbidity = 56 NTU TOC = 137.8 mg/L DOC = 496 mg/L	CN = 0.08 mg/L pH = 7 Turbidity = 68 NTU TOC = 24.5 mg/L DOC = 118.5 mg/L	Laboratory	[110]
Air micro-nanobubbles	Mine effluent	T = 21 °C pH = 11.99 Turbidity = 170 NTU Conductivity = 4.06 mS/cm $DO \leq 0.1$ mg/L TS = 4740 mg/L TSS = 251 mg/L Pb = 51.3 mg/L Zn = 17.601 mg/L	T = 22 °C pH = 11.72 Turbidity = 15.93 NTU Conductivity = 2.39 mS/cm DO = 8.53 mg/L TS = 4120 mg/L TSS = 31 mg/L Pb = 0.98 mg/L Zn = 0.128 mg/L	Laboratory	[111]
O_3 + ultrasound	Synthetic water with surfactant	pH = 8.3 Sodium lauryl sulfate = 100 mg/L	pH = 8.3 Sodium lauryl sulfate = 16.7 mg/L	Laboratory	[112]
Ozone microbubbles	Synthetic water with As(III)	pH = 7 As(III) = 200 µg/L As(V) $\leq$ DL	pH = 7 As(III) $\leq$ DL As(V) = 200 µg/L	Laboratory	[107]

DL: Detection Limit; TOC: Total Organic Carbon; DOC: Dissolved Organic Carbon; DO: Dissolved Oxygen; TS: Total Solids; TSS: Total Suspended Solids.

More research is required to systematically evaluate the performance of O_3 microbubbles process with mine effluents at low temperatures and scaling-up conditions. Further techno-economic studies are also necessary prior to full-scale mine site applications.

3.3. Membrane Filtration

Membrane-based processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), vacuum membrane distillation (VMD), and forward osmosis (FO). A combination of these filtration techniques is often required to ensure good

performance and minimize clogging membranes. Membrane filtration processes treat a variety of contaminants, from suspended solids and colloidal material to more persistent and soluble ones as salinity [59,113].

The nature of contamination determines the type of membrane to be used for effective treatment. Direct membrane filtration, or FO, achieves good contaminant removal rates by reducing release rates and treatment costs [114]. In addition, VMD increases the recovery rate of permeate when used alone or in combination with conventional filtration types [115–117].

The operating principle of all these processes lies in the pressure gradient exerted on the membranes, commonly called transmembrane pressure (TMP) [113,118]. The feed can pass directly through the membrane but is usually recirculated at high speed on the face of the membrane (crossflow configuration) [118]. This type of operation is recommended because the turbulence generated causes erosion and makes it possible to reduce the accumulation of solids on the membrane [118]. Membrane processes, their separation mechanisms, the materials used to manufacture the membranes, and their typical treatment objectives are presented in Table 5.

Table 5. Technical characteristics of the different types of membrane process [113,118,119].

Process	Separation Mechanism	Material/Type	Typical Transmembrane Pressure	Process	Separation Mechanism	Material/Type
Microfiltration (MF)	Separation by sieving through macropores (>50 nm)	Polymer and inorganic/Porous	10–100	90–99+	Removal of suspended matter and coarse colloidal particles including microorganisms	Pore size Exclusion at the membrane interface
Ultrafiltration (UF)	Separation by sieving through mesopores (2–50 nm)	Polymer and inorganic/Porous	50–300	85–95+	Removal of coarse molecules in solution and colloidal particles in suspension including bacteria and macromolecules such as proteins	
Nanofiltration (NF)	Separation by a combination of charge rejection, diffusion of solubility, and sieving through micropores (<2 nm)	Polymer and inorganic/Dense	200–1500	75–90+	Removal of multivalent ions and specific charged or polar molecules	Solution Diffusion through the membrane
Reverse osmosis (RO)	Separation based on the difference in solubility and diffusion rate of water and solutes	Polymer/Dense	500–8000	60–90	Removal of low molecular weight compounds such as inorganic ions	

The membranes can be made of polymers based on materials such as polyacrylonitrile (PAN) and polyvinylidenediflouride (PVDF). The cost of these membranes is relatively low, and their life cycle is around seven years [113]. Inorganic membranes are more resistant to chemical and thermal stress than polymer-based membranes. They are divided into four categories according to their constituents: ceramic membranes, glass membranes, metal membranes, and zeolite membranes. These are mainly used for MF and UF [113].

Two types of membrane configuration dominate the saline water treatment market with NF and RO: spiral wound and fine hollow fiber commonly known as spiral wound (SW) and hollow fine fiber (HFF). SW elements are constructed with flat membrane sheets and materials that provide mechanical strength. The materials of these membranes can be cellulosic or non-cellulosic. Cellulose acetate membranes are composed of two layers

of different shapes of the same polymer; they are called asymmetric [120]. Composite membranes are two layers of different polymers separated from a porous substrate, which is often polysulphone [120]. The materials used in the manufacture of HFF can be polyaramide or a mixture of cellulose acetate. The membranes usually have an external diameter between 100 and 300 μm and an internal diameter between 50 and 150 μm. Saline water is inserted into the media from the outside of the HFF; by applying pressure, the permeate passes through and is then collected [120].

Clogging of membranes is the main problem related to their use. Indeed, the presence of elements that clog the pores of the membranes reduces their effectiveness and even their lifespan. For example, the presence of organic species and suspended matter can have a high clogging effect [121]. Calcium sulphate and calcium carbonate can also clog the membranes [122]. In the treatment of mine water, the main clogging elements were identified as Sb, Al, Si, and Na [119]. Pretreatment steps can help overcome this problem [119]. Higher water temperatures can reduce the clogging effect as the membrane pores expand. By expanding, contaminants can more easily pass through the membrane and, thus, reduce the quality of the permeate [123].

The membrane cleaning methods depend on whether the clogging is reversible or not. If the clogging is reversible, the use of physical methods such as a pulsed reverse flow with purge, vibrations with ultrasound, air, or CO_2 jets, or reverse permeation at regular intervals can clear the pores. This type of cleaning tends to have less impact on the degradation of the membranes and their lifespan than a chemical cleaning [118,122]. Chemical cleaning uses a chemical to react with the sealing layer to facilitate physical cleaning. The most used membrane cleaners are alkaline or acidic cleaners, surfactants, and saline solutions; their choice is related to the type of sealant [122]. The use of ozone also reduces clogging by organic matter [121,124]. The parameters to consider during chemical cleaning are product concentration, pH, temperature, pressure, flow rate, and cleaning time [122].

Reported efficiency of membranes for mine water at different scales is presented in Table 6.

For example, the MF and UF can be used to remove total suspended solids (TSS) and colloidal chemical oxygen demand as pretreatment prior to RO, which can remove salinity [59]. The management of RO reject is an important consideration because of its high TDS concentrations. A treatment of this brine can reduce the reject and can be used as byproduct with resale value [125]. The VMD technology that uses hydrophobic membrane and heat can be a good way to concentrate the RO brine and recover metals. The removal of 99.9% of TDS with VMD technology was reported. The mine water tested contained 2332 mg/L of TDS, 14.4 mg/L of Ca, 2.72 mg/L of Mg, 1.92 mg/L of Fe, and 3.38 mg/L of Al. Removal efficiency was higher than 95% for all these elements after 90 min [126]. The EC of the treated water could be lower than 50 μS/cm [116]. The VMD can be used as a treatment for low concentration of heavy metals and to achieve better performance than conventional treatment [127].

As newer technology, FO has promising potential for the desalination of high salinity mine water streams (60–240 g/L TDS). FO utilizes a thin film composite membrane and draws solutions to recover the metals. The principle of FO is based on the osmotic difference between a dilute feed solution (FS, i.e., contaminated water to be treated) and a more concentrated draw solution (DS, with higher osmotic potential than FS), which is diluted during the salinity treatment. The next step of the process—the separation of clean water from the diluted draw solution—is energy consuming and, as a result, the limiting and decisive step in FO overall feasibility. A crystallization process can then be used to recover the metals and salts after the separation [128]. The major advantages of FO for water recovery are the non-selectivity (high rejection of a wide variety of contaminants), less fouling of membrane, the simpler osmotic cells, and the overall lower cost (no external hydraulic pressure is applied for the water to cross the membrane relative to pressure-driven processes such as in RO) [128]. FO was found efficient in metal removal from acid

mine drainage close or over 98% using NaCl-DS [129]. However, with mine water, the reverse flux of ions from the DS into the FS, especially when they can react with feed solutes, could prove one of the major downsides of this process, in addition to the precipitation of some secondary minerals on the separating membrane when inorganic salts are used in DS (e.g., NH_4HCO_3) [129]. More recently, the FO membranes showed to be promising in power production by the pressure-retarded osmosis (PRO) process [130]. Notably, osmotic energy generation (using PRO) was proposed more than 70 years ago, but it was limited by the lack of effective membranes. As recently as 2009, a prototype plant was constructed in Norway, but the project was terminated in 2014 due to technology immaturity [131].

Table 6. Treatment efficiency using membrane filtration with mine water at different scales.

Treatment	Industry	Influent	Effluent (Permeate)	Scale	References
MF + NF + RO	Gold mine pressure oxidation process water effluent	pH = 1.46 EC = 28.07 mS/cm TSS = 571 mg/L TDS = 23 973 mg/L Cu = 156.8 mg/L Co = 40.01 mg/L Ni = 256.8 mg/L Ca = 487.6 mg/L Mg = 2561 mg/L Fe = 436.5 mg/L Mn = 105.5 mg/L Al = 348 mg/L As = 34.6 mg/L Total Acidity = 10.28 g $CaCO_3$/L Free Acidity = 6.89 g $CaCO_3$/L SO_4^{2-} = 21 480 mg/L	pH = 2.56 EC = 0.79 mS/cm TSS = 0 mg/L TDS = 192 mg/L Cu = 0.22 mg/L Co = 0.09 mg/L Ni = 1.24 mg/L Ca = 1.61 mg/L Mg = 11.96 mg/L Fe = 0.56 mg/L Mn = 0.13 mg/L Al = 0.63 mg/L As = 2 mg/L - - SO_4^{2-} = 270 mg/L	Pilot	[132]
NF	Acid mine drainage from abandoned mercury mine	Fe = 515 mg/L Al = 23 mg/L As = 6 mg/L Hg = 2.3 µg/L SO_4^{2-} = 2300 mg/L pH = 2.47 ORP = 592 mV DO = 3.3 mg/L	Fe = 7.5 mg/L Al = 1.7 mg/L As = 0.08 mg/L - SO_4^{2-} = 245 mg/L - - -	Pilot	[133]
MF + NF	Acidic bioleaching mining waste process	Co = 4.04 mg/L Ge = 1.33 mg/L Mo = 14.30 mg/L Re = 3.26 mg/L Cu = 54 mg/L Fe = 1980 mg/L Zn = 720 mg/L	Co = 0.04 mg/L Ge = 1.18 mg/L Mo = 0.39 mg/L Re = 2.96 mg/L Cu = 0.74 mg/L Fe = 15 mg/L Zn = 7.8 mg/L	Laboratory	[134]
RO	Final effluent of antimony mine in operation	Turbidity = 39.4 NTU TDS = 7910 mg/L Sb = 49.8 mg/L As = 0.038 mg/L Ni = 0.052 mg/L Zn = 0.052 mg/L Fe = 0.05 mg/L Cd = 0.0001 mg/L Cr = 0.001 mg/L Cu = 0.002 mg/L Pb = 0.001 mg/L	Turbidity = 1 NTU TDS = 218 mg/L Sb = 0.1 mg/L As = 0.001 mg/L Ni = 0.001 mg/L Zn = 0.001 mg/L Fe = 0.05 mg/L Cd = 0.0001 mg/L Cr = 0.001 mg/L Cu = 0.001 mg/L Pb = 0.001 mg/L	Industrial	[119]

ORP: Oxydo-reduction potential.

The use of membrane filtration processes is common in the field of desalination for drinking water but less in the mining field. In recent years, research has made it possible to apply this technology to mine water and obtain satisfactory results [135].

4. Challenges and Opportunities in Mine Water Treatment in Cold Climates

Additional challenges in cold climates mean that system designs for effective performance of mine water treatment must also properly integrate specific characteristics, including the following: (1) high sensitivity and limited resilience of ecosystems, (2) unusual faster dissolution of carbonates at low temperatures, (3) the increased salinity in response to the very narrow window of water flow (2–3 months/year), (4) high costs of freshwater, (5) enhanced detrimental impacts of salinity on treatment efficiency and solubility of minerals from the gangue, (6) accelerated clogging of membranes, (7) limited knowledge about the suitable management of residual materials in a continuously evolving context (e.g., the increasing thickness of the active layer of permafrost), and (8) slower kinetics of most of the chemical processes. The impact from the mixing of different effluents on aquatic toxicity is also a big challenge. All these challenges must be targeted for future research to ensure sustainable mining in the North.

Nevertheless, few opportunities are arising in relation to mine water treatment in cold climates. Energy production from salinity, such as osmotic power generation by PRO using seawater brine as the DS and wastewater retentate as the feed, showed potential as a renewable energy source [130,136]. The use of promising membrane filtration technologies can help to recover the metals and reduce the salinity. The membrane fouling with high calcium and sulfate concentrations (i.e., gypsum scaling) is still an issue with some membrane materials. Further studies are necessary to solve these issues [137]. Finally, some AOPs could limit the creation of residual salinity and allow the simultaneous treatment of mixed contaminants.

5. Conclusions

This paper provided an overview of the issues related to the removal of CECs from mine water, with focus on As, Mn, Se, salinity, thiosalts, xanthates, and N-based compounds (cyanides, NH_3-N, and SCN^-) in cold climates. The background concentrations of As, Mn, Se, salinity, thiosalts, xanthates, and N-based compounds in natural water were first discussed. The performance of AOPs and membrane filtration processes in CECs treatment in mine water were then emphasized. Further studies are required for optimal treatment performance under cold climate conditions and high flow rates, including field-scale tests. In the contemporary context, the mining industry's ability to strengthen its capacity to adapt to increasingly stringent criteria related to CECs is central to sustainable development. Such adaptation will necessarily depend on close collaboration between mining operators and scientists conducting applied research, and the challenges will most likely increase in complexity in the very near future, which highlights the critical need for intensifying research on the treatment of CECs.

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