

Minimizing Xanthate Impacts on Watercourses in Cold Climate – Review on Available and Potential Approaches

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Abstract

Xanthates are essential process chemicals used as collectors in sulfide ore flotation, but they may be toxic to aquatic organisms even at low concentrations. The primary ways of controlling xanthate impacts are species type selection, dosing optimization, and prolonging the delay times. These means may be adequate to decrease the concentrations to acceptable levels. However, in some cases, separate xanthate removal may be needed. Particularly this concerns mines at cold climates and mines with neutral and/or alkaline discharge waters because spontaneous xanthate degradation rates are slower. This paper summarizes the current knowledge about xanthate management and removal.

Keywords: Xanthate, cold climate, water treatment, water management

Introduction

Xanthates are used as collectors in the flotation process in sulfide mineral concentration. Xanthates are organic sulfur compounds that have a polar and a non-polar charged end. Metal-sulfides attach to the polar end, and the hydrophobic non-polar end rises to the water surface with air bubbles forming a froth that can be skimmed. The concentrate will have most of the xanthates, but residual xanthates will follow the tailings or effluent. (Lam 1999; Bach *et al.* 2016) Approximately 2 billion tonnes of ore are processed in flotation with xanthates per year, dosage generally ranging from 30 to 300 g t⁻¹ ore (Pearse 2005). Thus, xanthates constitute a considerable usage of chemicals.

Xanthates have been found to be harmful to aquatic organisms and they increase toxicity of metals. The degradation of xanthates produces highly toxic carbon disulfide (CS₂), which is rapidly volatilised from solution into air. (Lam 1999; Bach *et al.* 2016)

Xanthates degrade in warm and acidic water, especially at high xanthate concentrations. (Hawley 1977) Also, the presence of metal salts, such as copper, iron, zinc, or lead, catalyzes degradation. (Bach *et*

al. 2016) At mines in cold climates having low water temperatures and ice cover on tailings management facility (TMF) or recycle water facility, xanthates' slow degradation kinetics combined to site wide positive water balance may lead to noteworthy concentrations of xanthate residues in the discharge water. (Muzinda and Schreithofer 2018) The challenge may be emphasized at alkalic conditions due to lower xanthate degradation rates in neutral or alkaline water. (Walterson 1984; Fischer and Jarsjö 2023)

The risk of xanthate residues causing environmental impacts cannot be ignored at mine sites in cold climates as xanthate residues have been detected in the discharge water (Walterson 1984; Fischer and Jarsjö 2023), meaning that degradation has been inadequate in the mine water cycle. Additionally, the importance of controlling xanthate residues seems to be increasing as the Swedish regulator has recently set the first discharge limit for residual xanthate concentration in discharge water. (Umeå Tingsrätt 2022) In Finland, the Finnish Environment Institute has suggested monitoring of xanthate concentrations in discharges and in recipient waterbodies of selected mines and industrial plants. When

more data is available from monitoring, the need for national legislation will be evaluated. (Mehtonen *et al.* 2022)

Methods to manage the environmental risks related to residual xanthates are: 1) using environmentally least harmful xanthate species, 2) avoiding overdosing, 3) increasing water recycle rate between the concentrator and tailings management facility. Additionally, active water treatment processes can be applied to remove residual xanthates. For example, 1) oxidation and especially Fenton processes, 2) sorption, and 3) coagulation processes can be applied for xanthate removal.

Most of the studies related to xanthates discuss wet tailings deposition. However, dry tailing deposition methods are gaining popularity also in cold climate environments. In dry stacking, even more than 75% of process water can be reclaimed and circulated back to process prior to final deposition. This decreases the residence time of xanthates in the water cycle, which decreases spontaneous degradation, but also offers a more efficient method of managing xanthate containing water streams. Same methods of xanthate management and residual xanthate removal may be applied to wet and dry tailings deposition. In all cases, the precise execution of xanthate management needs to be planned site-specifically considering the individual characteristics of each mine, the prevailing weather, and the local environment.

Controlling Xanthate Concentrations

The most important means of decreasing environmental risks related to xanthates should be avoidance of overdosing. Correct dosage does not only decrease the risk of residual xanthate concentrations in discharge water, but also improves metal recovery and process selectivity (Rao and Finch 1989; Muzinda and Schreithofer 2018).

As an example, Cu-Pb-Zn ore flotation selectivity decrease has been observed due to degradation of copper collector Z-200 (Ozkan and Acar 2004).

Xanthate degrades spontaneously with time. Xanthate concentrations decrease due to degradation and dilution during their residence time in TMFs and mine site water storage facilities. The residence time may be sufficient to reduce xanthate concentrations to environmentally harmless levels. Seasonal variation influences the process water composition in cold climate. In wintertime, low temperatures, lack of xanthate destructing UV-light (especially under ice covered ponds), and a low amount of dilution may increase the concentration of xanthate in process water until spring flood. (Muzinda and Schreithofer 2018) In Sweden, highest xanthate concentrations in mine discharge water were observed during springtime, whereas the highest concentrations in water streams inside the mining facilities were observed during winter (Walterson 1984; Fischer and Jarsjö 2023)

The harmfulness of residual xanthates may be reduced by choosing chemicals with lower environmental risk compared to other alternatives. The harmfulness of xanthates is assessed in the environmental risk assessment with predicted no-effect concentration (PNEC), which varies between xanthate chemicals. If several applicable flotation chemicals are identified, the least harmful should be chosen.

PNEC is derived by dividing the lowest toxicity concentration by assessment factor (AF) (Okonski *et al.* 2021). Assessment factor reflects the uncertainty related to the experimental work behind the concentration value. In this comparison, SIBX and PAX have the highest PNEC values in freshwater, whereas SEX and PIAX have considerably lower values for intermittent release.

Table 1 PNECs of Xanthate Compounds (ECHA 2023).

Xanthate compound	CAS No.	AF	PNEC aqua, freshwater	PNEC aqua, freshwater (intermittent releases)
Sodium ethyl xanthate SEX	140-90-9	100	0.47 µg L ⁻¹	0.0001 mg L ⁻¹
Potassium ethyl xanthate PAX	2720-73-2	10	0.36 mg L ⁻¹	0.18 mg L ⁻¹
Sodium isopropyl xanthate SIPX	140-93-2	10	0.01 mg L ⁻¹	0.021 mg L ⁻¹
Sodium isobutyl xanthate SIBX	25306-75-6	10	1.4 mg L ⁻¹	0.7 mg L ⁻¹
Potassium isoamyl xanthate PIAX	928-70-1	1000	3.67 µg L ⁻¹	0.037 mg L ⁻¹

Substitution of xanthates with other flotation chemicals, such as ether diamines or phosphoric acid esters, have been studied with some promising results. However, the introduction of new chemicals with inadequately known properties and without any long-term observational data, whereas xanthates have been used for decades without major environmental impacts, introduces a host of new risks that are hard to evaluate. (Fischer and Jarsjö 2023)

Xanthates end up from concentration plant to TMF with tailings and, from there, recycle back to the process as reclaim water or migrate to other parts of the mine site water cycle. On site water cycle, xanthate containing water mixes with other water streams diluting xanthate concentrations. The loading of xanthate per ton of tailings transported to tailings pond is higher in slurry deposition than in thickened or filtered tailings deposition. In the case of thickened and filtered tailings, xanthate containing process water can be more efficiently circulated between concentration process and tailings thickener or filtration unit promoting lower xanthate concentrations. Recirculation rate should be kept as high as possible to reduce water discharge from the TMF and, thus, to contribute to reduced xanthate emissions to the environment.

Technologies for Residual Xanthate Removal

If the above-mentioned methods cannot be applied or they are inadequate to decrease the xanthate concentrations to environmentally acceptable concentrations, active xanthate removal may need to be applied. Xanthate removal is most efficient from concentrated solutions, e.g., in association with the concentration plant or before the point where TMF excess water is mixed with other mine site water streams. This will also help to minimise the amount of water to be treated. Concentrations are lower in the mine discharge water due to dilution and degradation of the chemical, but treatment of them can also be a good option, especially if xanthates can be removed together with other pollutants at the effluent water treatment facility. Some applicable methods for xanthate removal are presented below.

Oxidation

In oxidation processes, chemicals such as ozone or hydrogen peroxide are used for xanthate degradation. Alternatively, xanthate may also be oxidised by UV light. Oxidation processes aim at degrading the xanthates fully into harmless bicarbonate, sulfate, and water. The challenge with all oxidation methods is production of intermediate products that may be even more harmful than the parent substance, like highly toxic carbon disulfide (CS₂).

In laboratory experiments, potassium ethyl xanthate (PEX) has been degraded in 20 min with removal efficiency of 96.5 % using a UV_{185 + 254 nm} lamp and 74.8 % using a UV_{254 nm} lamp. The removal efficiency increases with time. In 75 min, the removal efficiencies were 99.9 % with UV_{185 + 254 nm} lamp and 97.9 % with UV_{254 nm} lamp. In these experiments, the PEX concentration was 100 mg L⁻¹ and pH 10. (Fu *et al.* 2019) The advantage of UV light is the simplicity of the process and lack of chemical usage. UV treatment is commonly used in applications such as disinfection of domestic water. Successful UV treatment requires that there is no turbidity in the water, which would impede the transmission of light.

Hydrogen peroxide (H₂O₂) has been shown to degrade ethyl xanthate (EX) up to 90% in 30 min. However, EX does not degrade to harmless substances by hydrogen peroxide alone. Reaction may be catalyzed by Fe²⁺ ions, which remove TOC. Use of Fe²⁺ alone has led to TOC removal up to 41% and accompanied by UV light up to 48% (García-Leiva *et al.* 2019). Chen *et al.* (2015) observed that H₂O₂ concentration influences the degradation, but pH does not.

Ozone (O₃) has been used to decompose sodium n-butylxanthate (SBX) to low concentrations in just 5 min. Ozonation alone increased the total degradation rate to 16.2-23.3%. With a combination of ozonation and visible UV light (VUV), the total degradation rate increased to 30.4-41.6% (Fu *et al.* 2016).

Sorption

Sorption is a general term for various molecule level processes that remove xanthates from dissolution using surface active particles, such as bentonite or activated carbon. In

comparison to oxidation processes, a major benefit is that none or considerably less intermediate products are formed.

Ethyl xanthate (EX) has been removed from solution in laboratory experiments using activated carbon (AC). Activated carbon removed up to 99 % of ethyl xanthate at concentrations below 268 mg L⁻¹. At higher concentrations, the removal efficiency was reduced. Also, high pH slightly reduced the efficiency of the material. (Salarirad *et al.* 2021)

Oliveira and Rubio (2009) tested zeolite for isopropylxanthate removal. They found that zeolite needed to be modified for efficient removal. With modified zeolite, 98% removal of xanthate was obtained. The adsorbent was collected from the water by flotation and required a low recycling rate of 20% (Oliveira and Rubio 2009). Also, applicability of bentonite as sorption material has been assessed in some studies. (Rezaei *et al.* 2018; Amrollahi *et al.* 2019)

Coagulation – Flocculation

Coagulation-flocculation is used for the removal of organic substances from solutions and has also been found to remove xanthate. Xanthate anions can form sparingly soluble compounds and precipitate, e.g., with iron, aluminum, and copper ions which can then be separated (Yuan *et al.* 2023).

A combination of ferric chloride and polymerised aluminum chloride has been shown to work effectively with polyacrylamide in removing xanthate from alkaline and turbid flotation waters. Also, use of ferric sulfate, polymerized ferric sulfate, and polyacrylamide have been effective (over 99% removal) in xanthate removal under neutral conditions. (Yuan *et al.* 2023)

Electrocoagulation

Çırak (2022) has investigated electrocoagulation for xanthate removal with aluminum, iron, and copper electrodes. 100 % removal was gained using a copper electrode at pH 9 and with electric current 0.6 A. Treatment produced Cu(I) ethyl xanthate or Cu(II) ethyl xanthate precipitates. Similarly, the iron electrode removed 82.3 %

of the xanthate at pH 6.5 and with electric current 0.6 A (Çırak 2022).

Biological Water Treatment

Using biological methods Chen *et al.* (2011) were able to remove 81.8% of n-butylxanthates in 8 days (Chen *et al.* 2011). High xanthate concentrations can inhibit microbial activity and the method appears to be more viable in treatment of dilute xanthate concentrations. It is deduced that the challenge of biological xanthate degradation is its retention time and low efficiency (Yuan *et al.* 2023) which may be emphasized in cold climate.

Conclusions

Xanthate concentration in mine discharge water can be controlled with several methods. Most applied methods are: 1) avoiding overdosage of the chemical, 2) promoting long residence times in water ponds and in TMF to enhance spontaneous degradation, and 3) promoting closed water circulation between concentration plant and TMF. Furthermore, the environmental impact may be decreased by selecting the least harmful xanthate type. If these methods are inadequate to decrease the discharge water xanthate concentrations to environmentally safe concentrations, active water treatment techniques can be applied to assist xanthate removal.

Degradation of xanthate by oxidation is currently one of the most favored techniques. Its challenge is the tendency to produce intermediates having even higher toxicity than xanthate itself. Hydroxyl radical producing advanced oxidation processes were often seen as a better alternative because they degrade the compound further. Also, a variety of adsorbents have been developed for xanthate removal. The advantage of sorption is that it does not form intermediates. Also, coagulation-flocculation and biological processes have been developed for xanthate removal.

Treatment process for xanthate removal can be applied to concentration plant process water, TMF discharge water, or mine site discharge water. Water treatment efficiency may be limited in treatment of dilute water streams.

References

- Amrollahi A, Massinaei M, Zeraatkar Moghaddam A (2019) Removal of the residual xanthate from flotation plant tailings using bentonite modified by magnetic nano-particles. *Miner Eng* 134:142-155. <https://doi.org/10.1016/j.mineng.2019.01.031>
- Bach L, Dyrmosø Nørregaard R, Hansen V, Gustavson K (2016) Review on Environmental Risk Assessment of Mining Chemicals Used for Mineral Separation in the Mineral Resources Industry and Recommendations for Greenland. Scientific Report from DCE - Danish Centre for Environment and Energy no. 203. ISSN 2245-0203.
- Chen S, Gong W, Mei G, *et al* (2011) Primary biodegradation of sulfide mineral flotation collectors. *Miner Eng* 24:953-955. <https://doi.org/10.1016/j.mineng.2011.01.003>
- Chen X Hua, Hu Y Hua, Peng H, Cao X Feng (2015) Degradation of ethyl xanthate in flotation residues by hydrogen peroxide. *J Cent South Univ* 22:495-501. <https://doi.org/10.1007/s11771-015-2548-0>
- Çirak M (2022) Performance evaluation of electrocoagulation using aluminum, iron and copper electrodes for removal of xanthate. *Chemical Papers* 76:3661-3677. <https://doi.org/10.1007/s11696-022-02120-4>
- ECHA (2023) REACH - Registration, Evaluation, Authorisation and Restriction of Chemicals Regulation. In: <https://echa.europa.eu/fi/information-on-chemicals/registered-substances>
- Fischer S, Jarsjö J (2023) Flotation chemicals at Swedish mines Review of their potential environmental impact Flotationskemikalier vid svenska gruvor Sammanställning över deras potentiella miljöpåverkan. Stockholm University Department of Physical Geography.
- Fu P, Feng J, Yang H, Yang T (2016) Degradation of sodium n-butyl xanthate by vacuum UV-ozone (VUV/O₃) in comparison with ozone and VUV photolysis. *Process Safety and Environmental Protection* 102:64-70. <https://doi.org/10.1016/j.psep.2016.02.010>
- Fu P, Li G, Wu X, *et al* (2019) UV185₂₅₄ nm photolysis of typical thiol collectors: Decomposition efficiency, mineralization and formation of sulfur byproducts. *R Soc Open Sci* 6. <https://doi.org/10.1098/rsos.190123>
- García-Leiva B, Teixeira LAC, Torem ML (2019) Degradation of xanthate in waters by hydrogen peroxide, fenton and simulated solar photo-fenton processes. *Journal of Materials Research and Technology* 8:5698-5706. <https://doi.org/10.1016/j.jmrt.2019.09.037>
- Hawley JR (1977) The use, characteristics, and toxicity of mine-mill reagents in the province of Ontario. Ontario Ministry of the Environment
- Lam K-S (1999) Biodegradation of xanthate by microbes isolated from a tailings lagoon and a potential role for biofilm and plant/microbe associations. University of Western Sydney, Nepean
- Mehtonen J, Siimes K, Leppänen M, Junttila V, Äystö L, Vähä E (2022) Vesiympäristölle vaarallisten ja haitallisten aineiden asetuksen (VNa 1022/2006) 12 §:n mukainen suunnitelma [in Finnish]. Draft 15.11.2022
- Muzinda I, Schreithofer N (2018) Water quality effects on flotation: Impacts and control of residual xanthates. *Miner Eng* 125:34-41. <https://doi.org/10.1016/j.mineng.2018.03.032>
- Okonski AI, MacDonald DB, Potter K, Bonnell M (2021) Deriving predicted no-effect concentrations (PNECs) using a novel assessment factor method. *Human and Ecological Risk Assessment: An International Journal* 27:1613-1635. <https://doi.org/10.1080/10807039.2020.1865788>
- Oliveira CR, Rubio J (2009) Isopropylxanthate ions uptake by modified natural zeolite and removal by dissolved air flotation. *Int J Miner Process* 90:21-26. <https://doi.org/10.1016/j.minpro.2008.09.006>
- Ozkan SG, Acar A (2004) Investigation of impact of water type on borate ore flotation. *Water Res* 38:1773-1778. <https://doi.org/10.1016/j.watres.2003.12.036>
- Pearse MJ (2005) An overview of the use of chemical reagents in mineral processing. *Miner Eng* 18:139-149. <https://doi.org/10.1016/j.mineng.2004.09.015>
- Rao SR, Finch JA (1989) A review of water re-use in flotation. *Miner Eng* 2:65-85. [https://doi.org/10.1016/0892-6875\(89\)90066-6](https://doi.org/10.1016/0892-6875(89)90066-6)
- Rezaei R, Massinaei M, Zeraatkar Moghaddam A (2018) Removal of the residual xanthate from flotation plant tailings using modified bentonite. *Miner Eng* 119:1-10. <https://doi.org/10.1016/j.mineng.2018.01.012>

- Salarirad MM, Behnamfard A, Veglio F (2021) Removal of xanthate from aqueous solutions by adsorption onto untreated and acid/base treated activated carbons. *Desalination Water Treat* 212:220–233. <https://doi.org/10.5004/dwt.2021.26683>
- Umeå Tingsrätt (2022) Tillstånd enligt miljöbalken till fortsatt och utökad gruvverksamhet vid Tapuli, Palotieva och Sahavaara gruvor med tillhörande verksamhet vid Kaunisvaara anrikningsverk, Pajala kommun. 2022-12-01. Mål M 2090-19. [in Swedish]
- Walterson E (1984) Effects from xanthates at Swedish mineral enrichment plants (Swedish title: Effekter av anrikningsreagenser -Fördelning och spridning av xantater och xantatderivat vid anrikningsverk) Institutet för vatten- och luftvårdsforskning No. 748
- Yuan J, Li S, Ding Z, *et al* (2023) Treatment Technology and Research Progress of Residual Xanthate in Mineral Processing Wastewater. *Minerals* 13:435. <https://doi.org/10.3390/min13030435>