

THE RELEVANCE OF ALTERNATIVE LIXIVIANTS WITH REGARD TO TECHNICAL ASPECTS, WORK SAFETY AND ENVIRONMENTAL SAFETY

Stephen Gos, Andreas Rubo

Degussa AG, Rodenbacher Chaussee 4, 63457 Hanau, Germany, prepared by CyPlus® (www.cyplus.com)

ABSTRACT

Over the past couple of decades several endeavours have been made to develop lixivants with the intention of replacing cyanide in gold leaching. In 1980's these endeavours were largely economically driven, due to cyanide shortages at that time. In more recent times, the driving force has shifted to occupational health and environmental considerations. It is often argued that the high acute toxicity of cyanide alone makes it worthwhile considering to replace it completely by less toxic alternative lixivants. This has led to having to consider more criteria in the choice of any alternative lixivants, which have often not been taken into account in the past. The intention of this paper is to review these alternative lixivants and also review the criteria, which have ultimately led to most of these lixivants never having found any large scale application, if they passed laboratory stage at all. It is also intended to show, that by handling and treating cyanide in a proper manner, the overall profile for the use of cyanide compared to these alternative lixivants is very favourable. The question to really be answered is whether there is actually any chemical or process applicable to gold leaching that does not show the high toxicity potential of cyanide and that is still favourable with regard to looking at a broader spectrum of criteria and not only acute toxicity.

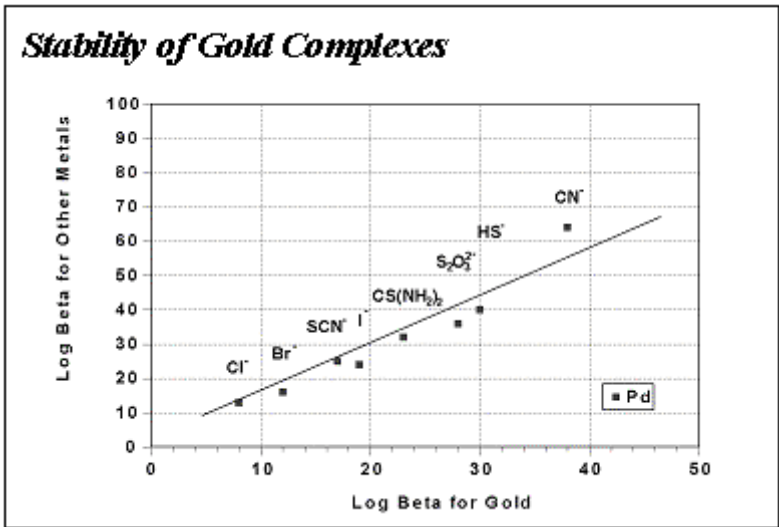
INTRODUCTION

The following is a list of alternative lixivants that have gained recognition in the literature and partly even up to large-scale applications over the last two decades.

All of these lixivants have the ability of being able to form water-soluble gold complexes under various conditions. The good solubility of these complexes in aqueous solutions is of utmost importance for any of the leaching processes to be viable. However, these gold complexes are of different thermodynamic stability according to the following figure:

The Alternatives are:

- 1 Thiourea
- 2 Thiosulphate
- 3 Thiocyanate
- 4 Bisulphide
- 5 Ammonia
- 6 Halogens
- 7 Malononitrile



As a consequence of these different stabilities, it can be said, that only the ligands with sufficient thermodynamic stability as cyanide can really be looked at as being alternatives with regard to chemical considerations. In all of the cases, it was at least expected and hypothesised that the gold complexes could be separated using activated carbon or resins in a plant very similar to a standard CIP or CIL plant. However, in some cases recomplexing with cyanide to enable separation has been reported, implying that the separation step (e.g. adsorption) would also have to be studied in more detail to enable a conclusive assessment of its performance for any alternative lixiviant. This is also an important aspect to consider if only the lixiviant should be replaced and not the whole plant design changed. Because most of these alternative lixiviants never passed laboratory or pilot plant scale, a closer look should be taken at the criteria which should be considered for the choice of any gold lixiviant for the gold mining industry today to explain the extremely limited applications. The following table lists some suggested criteria categorised into economics, process applicability and toxicity.


Which criteria should be considered for gold lixiviants?

Economics

- Capital Investment
- Extraction Economics
- Availability
- Costs Considering Detox/Recycling

Process Applicability

- Limitations (e.g. ore type, selectivity, control, separation)
- Recyclability
- Detoxifiability
- Large Scale Applications (proven technology)



Toxicity

- Emissions
- Handling (e.g. TLV and LD₅₀)
- Environmental Toxicology (e.g. LC₅₀)

In other words, it would be desirable that an ideal lixiviant be economical, universally applicable on most ore types and safe to transport, handle and detoxify or recycle. It should be mentioned at this stage, that any lixiviants operating in the acidic (e.g. thiourea) or even neutral pH range will tend to mobilize any metals present like copper or iron to a greater extent compared to a lixiviant operating in the alkaline pH range (e.g. cyanide). This can have the disadvantages of less selectivity for gold leaching, higher reagent consumption, because these metals are also leached, and higher treatment costs for any resulting effluents.

In order to be able to generate a profile, as a basis of comparison of these lixivants using these criteria, the possible individual advantages and disadvantages of the alternative lixivants should be discussed in more detail.

Before this is done, it is important to distinguish between the various kinds of toxicities (see figure 11). Taking the handling of a particular lixiviant as one of the criteria, the lethal dosage (e.g. LD50) as well as the occupational health standard e.g. TLV (or here the German equivalent: MAK) can be considered to yield indications as to how difficult the lixiviant is to handle safely. It should always be kept in mind that these toxicity criteria do not mean much, without simultaneously considering the question of exposure to the chemical and the products formed from its processing and treatment.

On the other hand, the criteria for ecotoxicity can be indicated by lethal concentrations for aquatic life (e.g. LC50) and the categorisation of the lixiviant into classes of water contaminants. The latter exists in Germany and is called WGK (Wassergefährdungsklasse). It is useful as a broad categorisation (0 = not a water contaminant, 1 = slight water contaminant, 2 = water contaminant, 3 = strong water contaminant). The ecotoxicity data are important in cases of the lixiviant accidentally entering any natural waterways (e.g. dam failure and transport incident) or for meeting water regulatory criteria.

Another aspect that should be mentioned at this stage is that it is not only important to consider the actual lixiviant itself, which is chemically always an anion. Considering any lixiviant always requires looking at the complete substance. This means that one also has to consider the toxicity profile and potential exposure scenarios of the corresponding cation. In most cases, the cation is sodium, but it can also be ammonium. This can change the whole perspective significantly as we will see in the case of thiosulphate leaching. In the following, it is endeavoured to illustrate in more detail, which criteria are of major importance for the alternative gold lixivants listed above.



THIOUREA

The capital costs should be similar to that of a cyanidation plant, although more expensive tanks (e.g. stainless steel) may be required to accommodate lower pH values. With regard to the extraction economics Yüce et al [1] reported values of up to 47 kg thiourea/t ore as well as extra costs for ferric sulphate and acid. Earlier work performed by Schulze [2] reported consumptions as low as 0.5 kg thiourea/t ore using SO₂ as a reducing agent. In general, the reagent consumptions reported in the literature seem to be considerably higher than that of cyanide, thus resulting in higher extraction costs. Thiourea, being a high volume chemical, has a high availability. The operating costs considering a detoxification step would be considerably higher compared to cyanide, because of the high chemical oxygen demand that would be necessary for full oxidation, alone due to the higher absolute demand of thiourea compared to cyanide.

Although Hiskey and DeVries [3] reported leaching rates 10 times faster than cyanide, the selectivity for gold is questionable. Due to the gold leaching reaction being very sensitive to pH and the redox potential, thiourea is intrinsically unstable and decomposes rapidly to substances that are unable to leach gold and has a toxicity profile that is no more favourable than cyanide. The chemistry of thiourea in this process is basically difficult to control with regard to optimal selectivity for gold leaching, since many possible side reactions are able to occur to products that do not leach gold. Formamidine disulphide is formed in the presence of an oxidising agent in the leach. This can produce cyanamide, hydrogen sulphide and elemental sulphur by irreversible reactions, thus increasing the necessary demand of thiourea. If the oxidation potential is not high enough, the ammonium ion and thiocyanate is formed in significant quantities (Yüce et al [1]). This would be of potential concern when considering the toxicity profile. This decomposition would also limit its recyclability, although a complete detoxification would seem to be possible but extremely expensive. Nevertheless, this is the only alternative lixiviant that has found some large scale applications as reported in Australia, China and France (Miner Eng. [4]).

Perhaps the biggest drawback that thiourea has experienced is that it has been categorised as a suspected carcinogenic compound and a water contaminant (WGK=2). Release of H₂S and NH₃ in higher quantities is also possible from the reactions mentioned above.

On an economical basis compared to cyanide, thiourea will remain a less attractive alternative lixiviant to cyanide, because of the higher reagent costs (especially if it has to be detoxified) and capital costs and its limitations with regard to being only suitable for certain ore types. With regard to toxicity, there is also no advantage to be seen, since thiourea is classified as a suspected carcinogenic compound for humans. This leads to the consequence that, according to occupational health considerations, a similar or even higher safety standard would be required to enable safe handling. The requirements for this high safety standard by far outweigh the seemingly low toxicity based on lethal toxicity and ecotoxicity data (see figure 11).

<p>Thiourea</p> $\text{Au} + 2\text{CS}(\text{NH}_2)_2 = \text{Au}(\text{CS}(\text{NH}_2)_2)_2^+ + \text{e}^-$  <p>+ Possible Advantages</p> <ul style="list-style-type: none"> ▪ Proven technology ▪ Availability ▪ Suitable for refractory ores ▪ Consumption has been reduced by redox control ▪ Fast rate of gold dissolution 	<p>Thiourea</p>  <p>- Possible Disadvantages</p> <ul style="list-style-type: none"> ▪ Limited recyclability (decomposition) ▪ Detoxification costs would be considerable ▪ Difficult to control process parameters ▪ Limited applicability
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THIOSULPHATE

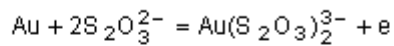
The capital costs for a thiosulphate leach plant could be assumed to be similar to that of a cyanidation plant. Although high reagent consumptions up to 48.6 kg/t ore have been reported by Yen [5] consumptions of 5 kg/t ore have been reported by Wan [6] on a carbonaceous (both as ammonium thiosulphate). The availability of thiosulphate is, however, high and reasonable in price, but the high reagent consumptions would indicate extraction economics much higher than that of cyanidation, even if ammonium thiosulphate is used (the price of sodium thiosulphate is approximately twice that of ammonium thiosulphate) and even if the lower range of consumptions is taken. If detoxification by oxidation is considered, the chemical oxygen demand would, however, be considerable and would increase these operating costs significantly, since four moles of active oxygen are required per mole of thiosulphate to obtain sulphate.

The main limitation of thiosulphate would seem to lie in its applicability (most testwork had been performed on carbonaceous ore types). Similar to thiourea, the leach reaction is very sensitive to pH and redox potential. Thiosulphate is also intrinsically metastable and decomposes readily to sulphate via a series of sulphur-oxygen species (mainly tetrathionate) and sulphide. Therefore, its recyclability would not seem to be possible. However, oxidation (detoxification) to sulphate is ultimately possible, but this would be extremely costly. The use of thiosulphate as an alternative lixiviant has passed laboratory scale to a pilot scale heap in an application in Nevada, USA (Wan [6]).

One apparent advantage of the use of sodium thiosulphate would seem to be its relatively low lethal toxicity and ecotoxicity, which could be argued on the lack of extensive LD50 (subcutaneous, rabbit, 4000 mg/kg) and LC50 (fish, > 10000 mg/l, exposure time not reported) data (only one example of each was found in the literature). This has to be at least confirmed with more extensive data, before a final judgement can be made. Although sodium thiosulphate is a recognised reducing agent for drinking water in Germany, its concentration is not allowed to exceed 2.8 mg/l of thiosulphate (German drinking water standard, Trinkwasserverordnung). Moreover, sulphide and bisulphide are spontaneous decomposition products of thiosulphate, which are highly toxic (see bisulphide as an alternative lixiviant and toxicity data). Sodium thiosulphate is also a reducing agent, with the potential to reduce the oxygen concentration in any natural waterway. In addition, in the case of a spillage into a natural waterway, the decomposition to sulphide or bisulphide (depending on pH) can occur, with the consequence of exceeding the ecotoxicity limits (e.g. LC50) for aquatic forms of life. Furthermore, its application in the literature has mostly been described in conjunction with its cheapest source, namely ammonium thiosulphate, to enable this process to become in some way economically viable. To be quite objective, however, the toxicity profile of ammonia and ammonium compounds must also be considered for ammonium thiosulphate. The use of ammonia as a lixiviant and its toxicity is described in more detail below. The result has the consequence for thiosulphate that it is either economically more viable (but still less so than cyanide) or environmentally acceptable, but not both, depending on whether ammonium or sodium is used as the cation for thiosulphate.

Compared to cyanide, thiosulphate can only be considered to be in any way economical, if ammonium thiosulphate is used and if it does not have to be detoxified. This, however, brings in the toxicity of ammonium compounds.

Thio sulphate



+ Possible Advantages

- Proven technology
- Availability
- Suitable for refractory/peg-robbing ores not amenable to cyanidation
- Good leach performance (e.g. >99 %)

Thio sulphate

- Possible Disadvantages

- Recyclable only to limited extent due to instability
- Detoxification costs would be considerable
- Control difficult
- Limited applicability



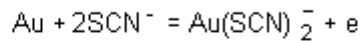
THIOCYANATE

Thiocyanate has been known to act as a lixiviant for gold for a long time. Not considered here is the mechanism by formation of the cyanide ion itself in the acidic and neutral pH range in the presence of an oxidant like hydrogen peroxide. More recently, Barbosa-Filho and Monhemins [7] showed that thiocyanate can leach gold in the pH range of 1 - 3 at higher temperatures (up to 85 °C). The low pH and the higher temperatures would indicate that high capital costs would be required for a leach plant. The higher temperatures would also mean that higher operating costs would be required compared to cyanidation. The availability of thiocyanate may also be a restriction and if thiocyanate had to be detoxified, a considerable oxygen demand would be necessary, which would even further increase the operating costs.

This lixiviant, however, may be suitable for most ore types and the recyclability could be possible if the temperature is not too high to decompose to a considerable extent. In practice, high temperature around 85 °C is, unfortunately, necessary to achieve satisfactory leach performance. An ultimate oxidation to cyanate and sulphate is also possible. These costs, however, as already mentioned, would be considerable, since five moles of active oxygen are required per mole of thiocyanate to oxidise it to sulphate and cyanate. No large-scale applications of this process could be found in the literature. With regard to safe handling, the apparent advantages would be that the LD50 is relatively high (rat, oral, 764 mg/kg) and that there are no evident releases of gas. Thiocyanate itself is only classified as a slight water contaminant (WGK=1) and the ecotoxicity data is also quite favourable (see figure 11). Analogous to thiosulphate, if ammonium thiocyanate is used, as reported in the above literature source, then the toxicity of ammonia and ammonium compounds should also be considered (see ammonia as an alternative lixiviant).

Compared to cyanide, the use of thiocyanate as an alternative lixiviant is probably not economically viable, because of the high temperatures required, even if detoxification costs are not considered. Although specific cases of viability may be possible with high grade concentrates, for example, the operating costs would be the limiting factor for universal applicability. Probably for this reason, no large scale applications are known.

Thiocyanate



✚ Possible Advantages

- Can act as a lixiviant over a wide pH range
- Recyclable (partly)

Thiocyanate



— Possible Disadvantages

- Availability limited
- No large scale applications known
- Detoxification costs would be considerable
- Higher temperatures required

BISULPHIDE

Hunter et al [8] of YES Technologies described a visionary process using bisulphide as a lixiviant for gold. The extremely long retention times and closed system, that would probably be required, would mean high capital investment costs for such a leach plant. However, the availability and reasonable price of bisulphide and its sources indicate reasonable extraction economics and because H₂S is regenerated from sulphate using bacteria. The operating costs considering detoxification, however, would be very high, because a high chemical oxygen demand would again be necessary.

One of the limitations would seem to be the sole suitability of this process for bio-oxidised ore, because a sulphate ion source is required for bisulphide regeneration. This process is recyclable, but theoretically an oxidation to sulphate would also be possible, although this again would be expensive. No large-scale application of this process is known to the authors.

With regard to safe handling, one major drawback would seem to be the fact that H₂S is generated. Since H₂S has a MAK (=TLV) very similar to HCN (possible by product of cyanidation), the safety standard of such a process would have to be able to handle such a substance. There would, therefore, be no advantage compared to the use of cyanide with regard to occupational health considerations. H₂S has a MAK (=TLV) of 15 mg/m³. Bisulphide itself is categorised as a water contaminant (WGK=2).

Compared to cyanide, bisulphide does not offer any major technical advantages nor does it have such favourable lethal toxicity and ecotoxicity data to warrant a more favourable classification with regard to safe handling or environmental damage in the case of a spillage. The long retention times as well as the probably very high capital costs involved for the closed system necessary, would also lead to the economic viability being much less favourable than that of cyanide. This may be the main reason why no large scale application has ever existed.

The Alternatives are:

- ① Thiourea
- ② Thiosulphate
- ③ Thiocyanate
- ④ Bisulphide
- ⑤ Ammonia
- ⑥ Halogens
- ⑦ Malononitrile

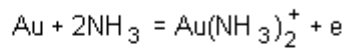
AMMONIA

Xinghui et al [9] have described the use of ammonia as a lixiviant for refractory ores at temperatures between 100 and 300 °C and 1.7 to 7.9 bar. The use of ammonia is more commonly known as an additional reagent in cyanidation for copper-containing orebodies. The high temperatures and pressures required would indicate high capital investment for a leach plant of this type. Although fast reaction times of 2 - 4 h were reported for 88 - 95 % recovery, the operating costs would seem to be prohibitive due to the high temperatures and pressures alone. The availability of ammonia and its price, however, would not be a restriction. Ammonia would have to be recycled and could not be detoxified easily. This reagent may even be suitable for most ore types, but not be selective with regard to leaching especially for copper-bearing orebodies. This is due to the formation of copper tetraamine from most copper minerals. The system would have to be closed to prevent the emission of ammonia. This is especially true with regard to upcoming air emission regulations like the Toxic Release Inventory (TRI) in the USA and the NPI in Australia.

Ammonia has a MAK (=TLV) of 14 mg/m³ and can, therefore, be classified very similar to HCN. The ammonium ion itself is classified as a slight water contaminant (WGK=1) and ammonia as a water contaminant (WGK=2). This means that ammonia and lixiviant containing ammonia or the ammonium ion can not be considered as a lixiviant having a more favourable profile regarding toxicity and exposure aspects.

The operating costs are the limiting factors in the implementation of this process, since high pressures and temperatures are required. Although this may be viable in isolated cases (e.g. very high grade concentrates), the capital and operating costs seem to be prohibitive compared to the use of standard cyanidation technology. Whereas cyanide will only form hydrocyanic acid gas to a more significant extent at a lower pH, ammonia gas is released, the higher the pH. In both cases the pHs for leaching are reported above 9. Therefore, ammonia would have to be a closed system to avoid the release of ammonia, even if high temperatures and pressures were not required. With regard to safe handling and environmental friendliness, the toxicity data in figure 11 do not warrant categorizing ammonia into a more favourable position than cyanide in either case. Ammonia may eventually be broken down to nitrate in the environment by bacterial oxidation, but this is a slow process. However, the economic viability seems to be the limiting factor in this process not having found any large scale application to date.

Ammonia



+ Possible Advantages

- Availability
- Recyclable
- Could be suitable for refractory ores

Ammonia



- Possible Disadvantages

- No large scale applications known
- Not detoxifiable: must be recycled
- Requires high temperatures and pressures for acceptable leach performance
- Selectivity doubtful

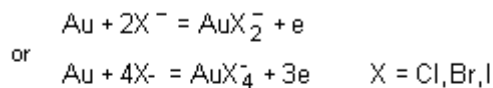
HALIDES / HALOGENS

Bromide, chloride and iodide, especially chloride, are well known lixivants for the leaching of gold. In the case of bromide and chloride, the extraction economics would seem to be reasonable. However, the use of an oxidant, usually the halogen of the halide itself, would lead to higher capital investment costs for the prevention of corrosion and the use of a closed system. The availability of the halogens would not seem to be a restriction, however, the halides, being ions, cannot be detoxified and would require electrical oxidation for recycling. The advantage of the use of halides / halogens would seem to lie in their universal applicability for most ore types as is the case with cyanidation. The use of chloride is a proven technology in gold refining. However, no current large scale applications of leach plants are known.

Perhaps the biggest drawback in the use of the halides / halogens lies in the handling. Workers' exposure to bromine and chlorine would be possible. The MAK (=TLV) value for Cl₂ and Br₂ are 1.5 and 0.66 mg/m³ respectively (iodine 1.1 mg/m³). Cl₂ is classified as a water contaminant (WGK = 2), Br₂ as a strong water contaminant (WGK = 3) and Br⁻, I₂ and I⁻ as slight water contaminants (WGK=1).

Compared to cyanidation, the economic viability has been reported to be similar, both with regard to the operating costs and the capital investment. It is, however, expected by the authors, that the electrical regeneration of the halogens and the closed system necessary would lead to less favourable economics. The limiting factor here is, however, that the oxidants used are mostly the halogen of the halides themselves, that all have MAK (=TLV) values much lower than that of hydrogen cyanide. It is also possible that they form halogenated organic compounds, that are usually very toxic even at very low concentrations. Therefore, halides can not be considered as favourable alternatives to cyanide.

Halogens



+ Possible Advantages

- Proven technology (e.g. Cl^- in Au refining)
- Availability
- Suitable for most ore types
- Leach performance is good (e.g. Br^- approx. 90 % < 4 h)

Halogens

- Possible Disadvantages

- Handling and control difficult
- Requires oxidant, mostly halogen or halide itself



LIXIVANT PROFILE

Based on the overview of the alternative lixivants above, it is possible to generate a lixiviant profile chart with the various criteria that should be considered in comparing any gold lixivants with cyanide. In light of the fact that one has to consider not only economical, but also environmental and sustainability considerations today, these criteria have grown in number and become more complex. This can be made clear with the example of emission regulations (in addition to existing waste water regulations, e.g. TRI) becoming of more relevance to the gold mining industry in the future. This, for example, could become very decisive in comparing alternative lixivants to cyanide, because it also makes it more difficult for these lixivants to fulfill all of the criteria that an ideal lixiviant should have with regard to economics, universal applicability, safe handling, environmental acceptability and regulations. Cyanide fulfills these criteria and the cyanidation process can be modified, without major investment or operating costs, to comply with all of these criteria, even in the future. Simple pH control to prevent HCN emissions, cyanide detoxification and/or regeneration are all proven technologies for the cyanidation process. It is left to the reader to consider this lixiviant profile chart (figure 11) as a basis of comparison. The profiles have been generated as seen by the authors of this paper. It is, however, necessary to consider site-specific criteria, since transport or metallurgical considerations, for example, can vary considerably.

	Economics			Process Applicability				Toxicity			
	Capital Investment	Extraction Economics	Availability	Costs considering Recycling (Metric)	Limitations (e.g. energy, selectivity, control, impurities)	Recyclability	Detonability	Large Scale Applications (pilot or technology)	Emissions	Handling (e.g. ILC, LD50)	Environmental Toxicity (e.g. LC50, WGK)
1. Thiourea	Grey	Black	Grey	Black	Black	Black	White	Grey	Grey	Black	Black
2. Thiosulphate	Grey	Black	White	Black	Black	Black	White	Grey	Grey	White	Grey
3. Thiocyanate	Black	Black	Grey	Black	Grey	Grey	White	Black	White	White	Grey
4. Bisulphide	Black	Grey	White	Black	Black	Grey	White	Black	Grey	Black	Black
5. Ammonia	Black	Black	White	Grey	Grey	Grey	Black	Black	Grey	Black	Black
6. Halogens	Grey	Grey	White	Black	Grey	Grey	White	Grey	Grey	Black	Grey
7. Malononitrile	Grey	Grey	Black	Black	White	Black	Grey	Black	Grey	Grey	Black
8. Cyanide	Grey	White	White	Grey	White	White	White	White	Grey	Black	Black
	Favourable			Acceptable				Not Favourable			

In the following, the toxicity profile chart is represented. It is important to emphasise that any toxicological data only represents examples of often very extensive data and the values can only be compared on an empirical level. This is because different conditions are used to generate this data (for example the time of exposure is often different or not specified at all or species are often different). In the case of LD50 for sodium thiosulphate, for example, only one value was found, whereby the exposure time was not specified. The lack of extensive data is also a cause of concern in being able to judge the true toxicity of a substance.

	Remarks	Criteria for Acute Toxicity / Handling		Criteria for Ecotoxicity incl. Transport Spillages	
		LD ₅₀ /LC ₅₀ (Lethal dosage/concentration example)	MAK (German equivalent to TLV)	Water Contaminant Category (WGK)	LC ₅₀ /EC ₅₀ (Lethal concentration example)
Thiourea*	Assumed carcinogenic, possible emission NH ₃ [*] , H ₂ S	LD ₅₀ 1750 mg/kg (oral, rat) [11]	none	2 [11]	LC ₅₀ >100 g/l (pimephates promelas) [11]
Thiosulphate (Sodium)	Possible emission H ₂ S	LD ₅₀ 4000 mg/kg (subcutaneous, rabbit) [14]	none	0 [11]	LC ₅₀ >10000mg/l (fish, time not specified) [14]
Thiosulphate* (Ammonium)	Possible emissions H ₂ S, NH ₃ [*]	LD ₅₀ 2890 mg/kg (oral, rat) [11]	none	1 [11]	Consider ammonium/ammonia
Thiocyanate (Sodium)		764 mg/kg (oral, rat) [11]	none	1 [11]	EC ₅₀ >100 mg/l (selenastrum capricomatum) [13]
Thiocyanate* (Ammonium)		LD ₅₀ 15 g (oral, human) [11]	none	1 [11]	Consider ammonium/ammonia [11] (280 - 300 ppm/1 h killed sunfish, conditions not specified) [12]
Bisulphide (Sodium) N.B. Data based on H ₂ S	Possible Emissions H ₂ S, H ₂	LC ₅₀ 1500 mg/m ³ /14 min (inhalation, rat) [11]	15 mg/m ³ [11]	2 [11]	LC ₅₀ 1500 mg/m ³ /7 min (inhalation, fly) [12] EC ₅₀ <0.86 mg/l (fish) [11]
Ammonia*		LD ₅₀ 350 mg/kg (rat, oral) [12]	14 mg/m ³ [11]	2 [11]	LC ₅₀ 0.53 mg/l/96 h (onchorhynchus mykiss) [11]
Chlorine*		LC ₅₀ 293 ppm/1 h (inhalation, rat) [11]	1.5 mg/m ³ [11]	2 [11]	LC ₅₀ 0.05 mg/l (fish) [11]
Sodium Chloride		LD ₅₀ 3000 mg/kg (oral, rat) [11]	none	0 [11]	No data (drinking water 250 mg/l ion) [12]
Bromine*		LD ₅₀ 14 mg/kg (oral, human) [11]	0.6 mg/m ³ [11]	3 [11]	LC ₁₀₀ 10 mg/l/10 h (cladophora) [11]
Sodium Bromide		LD ₅₀ 3500 mg/kg (oral, rat) [11]	none	1 [11]	LC ₅₀ > 10000mg/l (drinking water <0.6 mg/l ion) [12]
Iodine		LD ₅₀ 14000 mg/kg (oral, rat) [11]	1.1 mg/m ³ [11]	1 [11]	LC ₅₀ 0.16 mg/l (goldfish) [11]
Sodium Iodide		LD ₅₀ 4340 mg/kg (oral, rat) [11]	none	1 [11]	LC ₅₀ 10000 mg/l (drinking water <0.34 mg/l ion) [12]
Malononitril*	Explosive on heating, possible emission HCN*	LD ₅₀ 61 mg/kg (oral, rat) [11]	5 mg/m ³ (OSHA calculated as CN) [12]	2 [11]	LC ₅₀ 1.6 mg/l/96 h (rainbow trout) [12]
Cyanide* (Sodium)	Possible emission HCN*	LD ₅₀ 6.4 mg/kg (oral, rat) [11]	5 mg/m ³ (calculated as CN) [11]	3 [11]	LC ₅₀ 0.083 mg/l/96 h (leponis marochinus) [11]
Cyanide* (Hydrogen)		LD ₅₀ 3.7 mg/kg (subcutaneous, rat) [12]	5 mg/m ³ [12]	3 [11]	LC ₅₀ 2.29 mg/l/96 h (casellus communis) [12]

* TRII listed

CONCLUSIONS

Considering the overall profiles of the above lixivants, it is not surprising that cyanide is still the most common, if not only universally applicable lixiviant for gold bearing ores. Due to the knowledge and experience gained in this proven technology, it would also seem easily possible to sustain its safe use by detoxification and/or recycling as well as emission reduction. Although still a challenge to the mining industry, it would not be very difficult to implement these changes, since all of these technologies are already proven and known.

In the case of cyanide, a standard technology with reasonable capital and extraction economics, availability as well as proven detoxification and recycling technologies and universal applicability is in place. The only concern according to the profile would seem to be with regard to its ecotoxicity, since it is also classified as a strong water contaminant (WGK=3), for example. Its occupational hazard levels (MAK = 5 mg/m³), however, is not as low as that of any of the halogens and really the same order of magnitude of that of ammonia (MAK = 14 mg/m³) and bisulphide (MAK hydrogen sulphide 15 mg/m³).

As a finishing thought the above profile for cyanide could be made more favourable, for example, by implementing cyanide detoxification and/or recycling technologies to minimise the potential hazard areas at a gold mine (e.g. detoxification before discharge to the tailings pond). As a more visionary thought, careful pH and cyanide control and perhaps covered leach tanks are possible methods of reducing HCN emissions to negligible levels and reducing the cyanide content in the effluent (Gos and Rubo [15], Rubo et al [16]).

Looking at aspects of emission, exposure as well as regulations and limitations, the above mentioned potential alternatives show no significant advantages in their own right. Therefore, no one of these substances can claim to be a real alternative to cyanide, even when only toxicity and exposure aspects are considered. All of these claimed alternatives still have to prove any advantages in practice.

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