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## **Living With Cyanide**

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### **Goldschmidt 2001**

May 20-24, 2001  
Roanoke, Virginia, U.S.A.

*(see page 8 for information)*

[http://cass.jsc.nasa.gov/meetings/gold2001/  
gold2001.1st.html](http://cass.jsc.nasa.gov/meetings/gold2001/gold2001.1st.html)

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## Living with cyanide

### 1. Introduction

In the previous issue of *The Geochemical News* (#104, July 2000), I summarized what the media and UNEP/OCHA reported about the recent environmental disaster in Eastern Europe and supplemented it with information from various sources. That first article forms part of the backdrop, part of the social context if you will, for the article you are looking at now. Cyanide plays the lead role in both articles, but this one pays more attention to cyanide itself. However, neither article should be regarded as an authoritative and/or complete review, but as an introduction for those of us who are not very familiar with cyanide and its significance. As a geochemist, however, you will instantly recognize that the characteristics that make cyanide so toxic, difficult to handle and difficult to analyze also explain why it is used so widely. What you may not know is that thermodynamics has rather limited control over cyanide behavior in nature and how many questions cyanide raises, for instance about its solubility.

The cyanide issue is indeed very complex. 'Cyanide decomposes as soon as it gets released and does not do much harm,' say some. 'Not true!' respond others. 'The chemistry of cyanide is has been studied extensively and is well-known,' report some. 'Very little is know about the behavior of cyanide, and researchers have only just started to study it in detail,' judge others. 'Cyanide does not accumulate in organisms,' say some. 'Is that really the case?' ask others. 'Cyanide is bad, bad, bad,' say some. 'Cyanide is not only bad,' counter others. The variety in opinions is also caused by the complexity of cyanide's chemistry, its biochemistry and its geochemistry. And on your point of view.

### 2. Use of cyanide - sources of cyanide contamination



Let's start with an open door: the mining industry uses a lot of cyanide. In 1989, the mining industry in the United States alone used about 70 million kg, but it used about 50 million kg in 1988 (Eisler, 1991 and references therein). The current number is bound to be much higher, but its value does not really matter, except for cyanide manufacturers such as DuPont. Cyanide is used as a flotation reagent in base-metal and gold mining (Bell, 1974), for instance to separate gold-rich pyrite from arsenopyrite, and in cyanidation, to extract gold and silver from ores during dump leaching, heap or column leaching. Cyanidation is still the method of choice for most of the world's gold mines.

Gold in rocks may occur in fractures and along grain borders, or enclosed in pyrite, arsenopyrite, chalcopyrite and other minerals. Oxidation of sulfide ores (weathering) may release some of the gold at the surface of an ore deposit and this is easily recoverable, as is placer gold. The remainder of the ore is usually crushed and then subjected to cyanidation. The cost goes up with the amount of mechanical processing, but gold is leached much quicker from finer material. Dump leaching involves, of course, uncrushed material but takes considerably much longer than heap

leaching, where the material is crushed first and placed on a leach pad next. In both cases, the cyanide solution is then allowed to trickle through the heap. Varieties with vats and columns use the same principle.

Refractory ores do not release their gold during cyanidation without special prior preparation, such as bioleaching, autoclaving (pressure oxidation), roasting (thermal oxidation), and chlorination. Gold that is part of sulfide minerals such as pyrite and arsenopyrite forms a major refractory ore category. Carbonaceous gold ores are another special category, because the carbon competes with the cyanide. Copper/gold ores require uneconomically high quantities of cyanide. Copper forms at least three complexes during cyanidation and hence consumes a lot of cyanide that is unable to complex gold. Examples of other 'cyanicides', as they are called, are pyrrhotite, natural organic acids, sulfates, and arsenates, (Fagan, 1998). Interested 'non-hardrockers' may want to check out books like Guilbert and Park (1986) and Evans (1995), for further details about ore geology.

The mining industry has used and still uses a wide range of processes. As our insights in environmental issues change, what is considered environmentally justifiable or not continues to change as well. What was perfectly alright ten or twenty years ago, may be considered very unfriendly to the environment today. And vice versa.

The cyanidation process involves dilute solutions of usually sodium or potassium cyanide and has been used commercially for over 100 years, with patents dating back to the end of the 19th century (Fagan, 1998; Hilton and Haddad, 1986; Johnson *et al.*, 1998). Even though the process has been used for so long, its mechanisms still are not fully understood (Fagan, 1998). Its general description is fairly simple. Gold ions are not abundant in aqueous solutions, but gold can be oxidized to Au(I) and Au(III). Oxygen can easily oxidize gold in alkaline cyanide solutions, where gold has a relatively low (-0.4V) oxidation potential (Fagan, 1998). The cyanide keeps gold in solution as  $(Au(CN)_2)^-$  (the only gold-cyanide complex involved in cyanidation) and thus prevents the formation of oxide layers (Hilton and Haddad, 1986; Haddad and Rochester, 1988).

Aqueous solutions of cyanide are actually not thermodynamically stable, but in the absence of catalysts and at high pH, oxidation to cyanate is very slow (Fagan, 1998). To prevent outgassing of HCN, the cyanide solution is kept at a pH well above the pKa of HCN (about 9.2), say 10.5. Lime or sodium hydroxide is used to control the pH (Fagan, 1998; Haddad and Rochester, 1988). Cyanide also removes other precious metals and base metals from ore. Zinc and copper are relatively weakly complexed by cyanide while gold, silver, iron and cobalt are strongly complexed. Kinetics plays a role as well, of course. Although cyanide complexes cobalt(II) strongly, as  $(Co(CN)_6)^{3-}$ , four steps are involved and the full complexation process is relatively slow (Fagan, 1998).

Cyanide can not only be lost through evaporation as HCN gas, but also through hydrolysis (oxidative pathways that break the C-N bond), conversion into thiocyanate, precipitation of cyanometallic compounds (notably with sulfidic ores), and adsorption/coprecipitation (notably with ferric oxides, in the case of oxidized ores). Stable-isotope tracers can be used to study these losses (Johnson *et al.*, 1998).



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areas near the coal mines used mine gas, but eventually, all the countries' stoves and heaters were converted for natural gas, after the Slochteren natural gas resources were discovered in the 60s. Gas plants were also built in the U.S. and other countries, where similar developments took place. The United Kingdom had at least about 3000 and possibly some 5000 MGP sites (Barclay *et al.*, 1998). The Netherlands had 234 (Didde, 1995; Meeussen *et al.*, 1994).

The nature and extent of the contamination often make the impact of mining spills appear much more devastating and much better known with the public. MGPs, however, are almost always located in highly populated residential areas, which means a higher potential risk for human beings and also results in high cleanup costs. Barclay *et al.* (1998) give a typical cyanide concentration range at MGP sites of 1 to 1,000 mg kg<sup>-1</sup> soil, but add that the concentration may be as high as 8,000 mg kg<sup>-1</sup> and give concentrations as high as 50,000 mg kg<sup>-1</sup> for sites in the State of New York.



Iron cyanides such as Prussian Blue have also been used in dyes, inks, cosmetics and other products for more than 150 years (Meeussen, 1994; Ghosh *et al.*, 1999a). Some drugs, for instance sodium nitroprusside, contain significant amounts of cyanide. Electroplating factories, zinc and aluminum smelters, and road salt storage facilities (cyanide is added as an anti-caking agent) are also often sources of potential cyanide contamination. In addition, cyanide has a wide range of 'household' applications, such as fumigation, pesticides, rodent control, and predator and pest control. An example of the latter are devices used by U.S. Fish and Wildlife Service Animal Damage Control Programs (Eisler, 1991), to keep populations of certain species in check. Pellets from these devices are known to also kill other species than those they were intended for (Eisler, 1991).

### 3. Analysis and speciation of cyanide

Nowadays, with the current environmental awareness, pollution laws and decision support systems often need concentrations to determine what action should be taken at a contaminated site. This has of course increased the need for reliable and detailed analyses and for spatial distribution data (Staritsky *et al.*, 1992). However, what is analyzed depends on the regulations and the purpose of the analysis. Cyanide determinations during heap leaching are done to assess whether the solution is still potent enough, and also to check if environmental regulations are complied with. Analysis for environmental purposes may be more detailed, but it still depends on who wants the analyses done and why. And on who does the analyses.

Free cyanide is HCN and CN<sup>-</sup> together. Dissolved HCN is a weak acid that dissolves and mixes very well in water. Cyanide ions are sometimes called pseudohalide ions, because their chemical behavior resembles that of halide ions. However, the term 'free cyanide' is not as clear-cut as it sounds and does not necessarily mean 'uncomplexed cyanide'. Weak-acid dissociable cyanide (WAD; Cu, Zn and Ni complexes) easily releases its cyanide, but not always that easily, otherwise copper would not be

such a problem during cyanidation. Particularly the presence of copper can distort analyses. While copper-complexed and zinc-complexed cyanide both may show up as 'free cyanide' in analyses of leach solutions, the copper-complexed cyanide is not available for leaching gold. On the other hand, copper-complexed cyanide may not show up in free cyanide analyses for environmental purposes and may mask a rising cyanide concentration. Fagan (1998) reviewed the stability constants of the three Cu(I) complexes that are formed during cyanidation: (Cu(CN)<sub>2</sub>)<sub>2</sub><sup>-</sup>, (Cu(CN)<sub>3</sub>)<sub>2</sub><sup>-</sup> and (Cu(CN)<sub>4</sub>)<sub>2</sub><sup>-</sup>. Organic compounds, sulfide, and zinc can also interfere with the analysis of 'cyanide' (Fagan, 1998; Haddad and Rochester, 1988; Hilton and Haddad, 1986). Strong-acid dissociable cyanide (SAD) includes the cyanide complexes of gold, silver, cobalt and iron. Fagan (1998) developed a reversed phase ion interaction chromatography method, which uses UV detection to measure individual metal complexes and a post column method (based on the König reaction) to determine free cyanide. There is in fact a large number of methods available for cyanide-related analysis, based on several techniques (titrimetry, spectrophotometry, AAS, spectrofluorometry, potentiometry and amperometry). While developments such as flow injection analysis and membrane diffusion greatly advanced analysis, most of these methods focus on either 'free' cyanide, 'total' cyanide, WAD, 'extractable' or 'amenable' cyanide. Covering them all would go too far here. Thorough analysis methods tend to be expensive and time-consuming and interpreting cyanide analyses is just as complicated as the analyses themselves. The quotation marks are meant to convey that working on practical analysis methods for 'cyanide', and perhaps also the interpretation of results, is another nice task for geochemists.

There are of course many more cyanide compounds than free, WAD and SAD. Examples are cyanate, hypocyanate, the nitriles (synthetic organocyanides), cyanogen and cyanogen chloride. The latter can for instance be formed when cyanide spills are treated with sodium hypochlorite. There are fewer methods to determine cyanate than cyanide: Kjeldahl Nitrogen method, electrochemically and colorimetrically (Fagan, 1998). Cyanate is less toxic than cyanide.

### 4. Toxicity

There is no question that free cyanide is highly toxic to almost all organisms. Cyanide is a very fast-acting poison, in a way comparable to adding a bit of sugar or sand to a gas tank. Under certain conditions, many but not all people can smell cyanide (the smell of bitter almonds). Of those who can, not everyone starts discerning it at the same concentration.

The symptoms of cyanide poisoning vary. The first stage may lead to headache, vertigo, weak yet rapid pulse, nausea and vomiting. The second stage is more alarming and may for instance include convulsions. The third stage is the final stage, leading to death, but cyanide poisoning does not automatically lead to death. Cyanide has a very steep dose-response curve (Kjeldsen, 1999), meaning that a little bit more can do a lot more damage. The body will detoxify relatively small doses of cyanide with little difficulty and any signs of poisoning will slowly disappear, with no remaining health effects. Cyanide can be exhaled as HCN and CO<sub>2</sub> in breath, and may react with cystine, and with vitamin

B12 (to cyanocobalamin). Probably most of the cyanide will react with thiosulfate, catalyzed by enzymes such as rhodanese, and is then excreted in urine as thiocyanate (Eisler, 1991). However, thiosulfate levels in the human body are usually low, and the amount of thiosulfate in the body and thiocyanate metabolism vary between individuals and species. Fish are very sensitive to cyanide, which is one of the reasons why cyanide is used to catch fish. Birds are less sensitive than fish but more sensitive than most other species. Cattle appear to be more vulnerable than sheep, horses and pigs (Eisler, 1991). The human body's response depends on the nutritional state of the person (vitamin B12 deficiencies) and on the specific cyanide compound it is dealing with. WAD is about as toxic as free cyanide. SAD is less toxic (Kjeldsen, 1999), simply because these complexes don't release cyanide as easily as WAD. Iron cyanide complexes, for instance, are about a factor 1000 less than cyanide and not surprisingly, appear to withstand the gastric acids as well (Kjeldsen, 1999; Meeussen, 1993). The toxicity of organic cyanide compounds varies, but is also basically related to the ease with which they release cyanide. The medical literature reports one case of cyanide poisoning from ingesting an organic solvent, acetonitrile. Thiocyanate is also much less toxic than cyanide but may accumulate in tissues and then create health problems (Eisler, 1991). Chronic cyanide poisoning is probably best known from detective stories, but is actually more common in areas where cyanide-containing plants, such as cassava, are staple food. No teratogenic, mutagenic and carcinogenic effects have been documented. Cyanide may have some therapeutic effects against some forms of cancers (Eisler, 1991).

Poisoning may take place via skin contact, via inhalation or via ingestion, although the latter is less common (Kjeldsen, 1999). Some snake venoms may produce HCN upon tissue destruction following injection. Cyanide poisoning may also result from exposure to smoke from a fire and from tobacco smoke. People who smoke and patients with renal insufficiencies just prior to dialysis have higher blood plasma thiocyanate levels (Eisler, 1991).

There are several antidotes for cyanide poisoning, for instance cobalt salts or a nitrite-thiosulfate combination, the choice of which is often according to local medical custom.

Let's move from organisms to the environment next: how does the environment metabolize cyanide?

##### 5. What happens to cyanide after it has been released?

With spills or leaks from mine sites, the first thing to happen is dilution. This is often the main attenuation mechanism. Complexed cyanide often remains mobile and does not adsorb, partly because it is negatively charged, as are most particle surfaces (Kjeldsen, 1999). The amount of light, the pE and the pH, the presence and amount of other compounds and elements, and the presence or absence and amount of certain microorganisms determine what happens further. Winter conditions are unfavorable, because evaporation and degradation are less in winter, for instance because UV light destroys cyanide (Meeussen *et al.*, 1989) and the UV intensity is less in winter. The pH is unlikely to be above the pKa of HCN and HCN therefore also volatilizes. Some cyanide will be converted to cyanate and other compounds. Iron complexes tend to be relatively harmless as long as they don't

break down. Basically, cyanide itself is probably best outgassed/converted and diluted. Outgassing is also a form of dilution, of course. The strongly complexed cyanide is perhaps best kept complexed, while the weaker complexes should be allowed to break down and converted to other forms as rapidly as possible. Gold cyanide complexes released from a gossan tailings pile in Canada were rapidly degraded (reduction of gold by divalent iron) and also converted into colloids (Leybourne *et al.*, 2000). The sediments and the water close to the source and at a distance contained high gold concentrations, but the size of the gold in water increased with distance from the source. The authors hypothesize that cyanide is oxidized and that this would fit in with higher nitrate concentrations found downstream. This would also indicate that cyanide persisted in the ground water over a considerable distance (Leybourne *et al.*, 2000). Finally, microbes also convert some of the cyanide (*s.l.*).

The situation is somewhat different at MGPs and other sites, where solids initially dominate, and where solubilities play a large role. Iron complexes are the main metal complexes at MGP sites, also because soil usually contains a lot of iron. In the dark, iron complexes are fairly stable. On exposure to daylight and perhaps specifically the UV part of the daylight spectrum, iron complexes decompose rapidly after which HCN gas is released. This should be controlled (not necessarily prevented) as much as possible, because it might increase the risk for residents. At the moment, it is not entirely clear which iron phases are formed at MGP sites. The solubilities of those phases determine the concentration of free cyanide to a large degree as well as the concentration of dissolved iron cyanide complexes.

Cyanide waste at former MGPs usually takes the form of iron cyanide compounds, where iron comes from the bog ore and from soil. The best-known iron cyanide solid is Prussian Blue ( $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ ), which is stable in an oxidizing environment (Ghosh, 1999a), but should dissolve at higher pH. Another well-known iron cyanide compound, Turnbull's Blue ( $\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$ ) dominates at lower pE (Ghosh, 1999a). These minerals share the same crystal structure (face-centered cubic), but have different proportions of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  (Ghosh *et al.*, 1999a). Prussian Brown, Berlin Green and Berlin White (phases with more extreme  $\text{Fe}^{2+}/\text{Fe}^{3+}$  proportions) are unstable. Meeussen and coworkers (1992c) performed the first extensive solubility study of Prussian Blue, but used outdated stability constants according to Ghosh *et al.* (1999a) (older NBS constants instead of more recent revised ones). Ghosh *et al.* (1999a) also object that the data of Meeussen and his coworkers do not pertain to equilibrium, because the reaction period was fixed and relatively short. They conclude that the solubility product for Prussian Blue reported by Meeussen and his colleagues has to be inaccurate. (Although I have included the Meeussen 1992c reference, I did not have this paper and the related data available when I wrote this article and was unable to assess this issue.)

Ghosh and his colleagues (1999a) used the program MINEQL<sup>+</sup> and its more recent stability constants to calculate the speciation of cyanide in equilibrium with  $\text{Fe}(\text{OH})_3$  (Fig. 3).  $\text{Fe}(\text{OH})_3$  was chosen because it is so common and because most

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soils contain large amounts of iron. The solubility of  $\text{Fe}(\text{OH})_3$  is also expected to determine to a large degree what happens to cyanide at former MGP sites. Precipitation and dissolution experiments carried out by Ghosh *et al.*, (1999a) yielded higher concentrations than calculated. Adding other iron cyanide phases to the MINEQL<sup>+</sup> model resulted in much lower calculated solubilities. Precipitation of cyanide with ferric oxides can also interfere with cyanidation, apparently lowering the solubility of cyanide under those conditions.

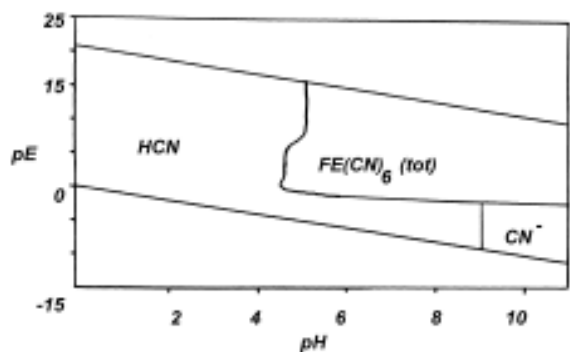


Fig. 2. Dissolved cyanide species in equilibrium with  $\text{Fe}(\text{OH})_3$ , according to Ghosh *et al.* (1999a). Calculated with MINEQL<sup>+</sup>. Total cyanide = 0.6mM; total iron = 0.5mM, total potassium = 0.4mM, total sodium = 0.06 mM, total chloride = 0.0612M and  $I=0.06\text{MNaCl}$ .  $\text{Fe}(\text{CN})_6(\text{tot})$  is complexed cyanide.

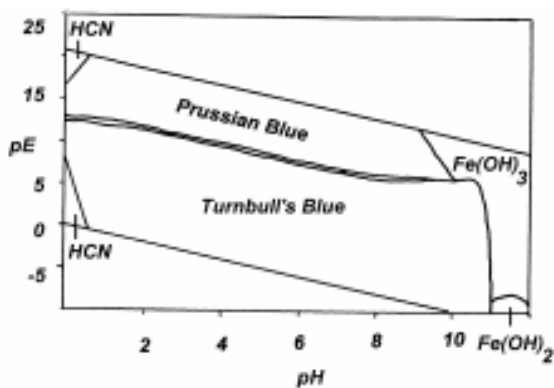


Fig. 3. *pE-pH* diagram for iron cyanide phases in water, without excess iron, according to Ghosh *et al.* (1999b). Calculated with MINEQL<sup>+</sup> using observed solubility products. Note the field where Turnbull's Blue and Prussian Blue coexist. Conditions in natural soils are usually restricted to the central part of this diagram.

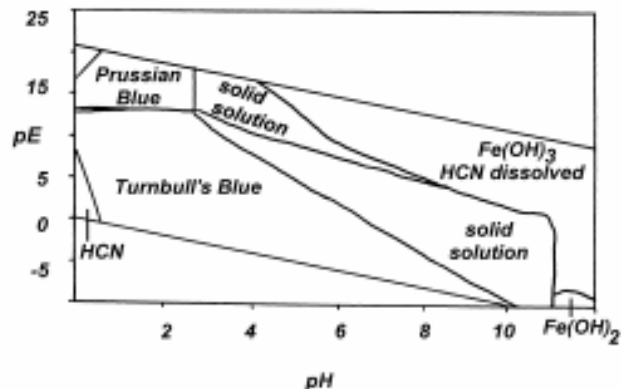


Fig. 4. *pE-pH* diagram for iron cyanide phases in water, in the presence of excess iron, according to Ghosh *et al.* (1999b). Calculated with MINEQL<sup>+</sup> using observed solubility products. Note again the field where Turnbull's Blue and Prussian Blue coexist. Conditions in natural soils are usually restricted to the central part of this diagram.

The increase in solubility in the presence of excess iron, found by Ghosh and his colleagues (1999a), rose with pH. The authors hypothesize that this may be caused by coprecipitation of iron hydroxide and iron cyanide, and that these precipitates may form a solid solution during the aging process. The conclusions from their work are that cyanide solubility increases with pH in iron-rich soils and is higher than in iron-poor soils (see Figs. 2, 3 and 4). Mixing or equilibrium may also exist with other phases, such as manganese iron cyanide, in that case leading to lower solubilities (Kjeldsen, 1999 and references therein).

Ghosh *et al.* (1999a) add that cyanate ( $\text{CNO}^-$ ) theoretically may dominate in highly oxidizing environments, but that conversion of cyanide into cyanate proceeds very slowly, unless in the presence of ozone or hydrogen peroxide (also stated by Fagan, 1998). Cyanate in turn will rapidly undergo hydrolysis.

Meeussen *et al.* (1994) use the solubility product for Prussian Blue from their earlier work, and also calculate dissolved iron cyanide concentrations in equilibrium with Prussian Blue and iron hydroxide, with the model ECOSAT. Their results indicate that at  $\text{pH} > 7$ , more than one mole  $\text{L}^{-1}$  would be in equilibrium with Prussian Blue (the solid). In other words, Prussian Blue would not precipitate.

At low pH and low pE iron generally tends to dissolve more easily (Meeussen *et al.*, 1994) and iron hydroxide is not expected to precipitate under those conditions. This was confirmed by experiments by Ghosh *et al.* (1999a). Precipitation of Prussian Blue is not expected in alkalic soils, but solid Prussian Blue was found at alkalic sites (Meeussen *et al.*, 1994, 1995). This may be due to slow dissolution kinetics, limitations by diffusion, a local acidic microenvironment created by dissolution of Prussian Blue, perhaps in combination with the influence of bicarbonate (Meeussen *et al.*, 1994). The alkalic sites did often have a lower pH (5.5) in the blue-colored top layer. The solubility of

Prussian Blue increases rapidly from almost zero at pH 4 to very high at pH 7. Meeussen and his coworkers (1994) hypothesize that dissolution of Prussian Blue may take place so slowly that Prussian Blue is able to persist for decades.

Ghosh *et al.* (1999b) studied an MGP site over a sand-gravel aquifer in the United States. They found more than 98% of the cyanide present as stable iron complexes (non-reactive). WAD, although only present in small proportions at this particular site, is expected to be more reactive and to undergo some form of degradation. Dilution appeared to be the main attenuation mechanism at this site, according to the authors, and this has also been found at other sites. Ghosh and his coworkers analyzed for total cyanide, WAD, free cyanide and in some cases (high cyanide concentrations) also for metal cyanide complexes (ion chromatography). They also attempted to characterize the spatial distribution of the contamination, as did Staritsky *et al.* (1992), for a former galvanic factory site in The Netherlands. This often helps to limit the cleanup costs.

Kjeldsen (1999) also discusses the discrepancy between calculated and measured free cyanide concentrations. Both Kjeldsen (1999) and Meeussen and coworkers (1994) arrive at the conclusion that iron-complexed cyanide degrades extremely slowly in soils in the dark, with half-lives ranging from decades to 1000 years (excluding microbial activity).

Besides uncertainties regarding the solution chemistry of iron cyanide compounds, there are also questions and discrepancies pertaining to the influence of daylight, UV or perhaps particularly the UV component of daylight, on the decay of iron cyanide complexes. The uncertainties also sometimes raise questions about experimental results (compare with choosing cells for UV-VIS spectrophotometry).

Containing the contamination can be very important if there is not enough natural attenuation and if the polluted site is located in a highly populated/residential area, as is usually the case with MGPs. Correct assessments and accurate predictions of cyanide behavior are needed to be able to deal with these sites as well as possible.

## 6. Cleaning up tailings solutions and remediating contaminated sites

The international community does not appear to agree on the treatment to be used after a spill. Cyanogen chloride may form after treatment with sodium hypochlorite. Hydrogen peroxide oxidizes cyanide into cyanate, which is much less toxic. In practice, it will probably mainly depend on what is available in what quantities, and on other local conditions. The methods will aim at immobilizing and containing the cyanide, converting it into a less toxic compound or both.

Several plants and organisms produce cyanide or cyanide-containing compounds, for instance as a defense mechanism. Partly as a response to the former, other organisms exist that either are able to neutralize this toxicity or actually use cyanide compounds as a substrate (Barclay *et al.*, 1998; White and Schnabel, 1998). The latter can be enlisted to help us tame cyanide on-site.

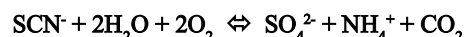
Barclay *et al.* (1998) report on metal cyanide degradation by fungi, which is relevant for MGP sites. These authors

isolated fungal cultures from MGP sites. A culture of *Fusarium solani* and *Trichoderma polysporum* was maintained on tetracyanonickelate. A mixture of *Fusarium oxysporum*, *Scytalidium thermophilum* and *Penicillium miczynski* was cultured on hexacyanoferrate. Both culture mixes were able to use  $K_4Fe(CN)_6$  as sole nitrate source, at acidic pH. The cultures also rapidly degraded  $K_2Ni(^{14}CN)_4$  at pH 7.

Cellan (1996) compared lab and commercial neutralization data for the Homestake Santa Fe mine. Barren solutions from the site were used to rinse spent ore from the mine's leach pads. In the lab, this process removed most WAD from the leached ore. The lab results apparently compared well with the actual site data. Cellan recommends lab tests that closely follow the conditions at the site, such as bed thickness, to be included in the planning of mines and mine closures.

Given and Meyer (1999) report on the tailings solution treatment applied at the Homestake Nickel Plate Mine in British Columbia. Cyanide, thiocyanate, ammonia and nitrate were removed by aerobic and anaerobic biological treatment, while a High Density Sludge (HDS) process was applied to remove metals. Breakpoint chlorination, hydrogen peroxide and the Inco SO<sub>2</sub>/air process are alternative methods, according to these authors. Breakpoint chlorination is the only process that also removes thiocyanate, ammonia and nitrate but it is very expensive and results in problematic high chloride concentrations. It turned out that the existing plant could be converted into a biological treatment facility with very little effort and expense. The treatment plant became operational in October of 1996.

According to Given and Meyer (1999), thiocyanate is converted by several bacteria, notably *Thiobacillus thiooxidans*, *Thiobacillus thioparus*, and *Thiobacillus denitrificans*, through addition of an organic carbon source, according to:



*Nitrosomonas* and *Nitrobacter* species use inorganic carbon and proceed with the conversion of ammonia via nitrite into nitrate. In this process, pH needs to be controlled, for instance with soda ash or lime. The nitrification process also requires temperatures of ideally 15°C or higher, oxygen needs to remain high enough and the high metal contents may interfere with the nitrifiers.

Cyanide and cyanate can be taken care of by species of *Pseudomonas*, *Alcaligenes*, and *Achromobacter*, and also with the help of *Chromobacterium violaceum*, which produces rhodanase. The resulting cyanate, also a product of the Inco SO<sub>2</sub>/air process and from WAD conversion, at neutral to acidic pH, can be hydrolyzed to form ammonia and bicarbonate.

WAD can be adsorbed onto biomass and then converted into cyanate. SAD can only be removed by precipitation (see also the sections on MGP sites).

*Pseudomonas*, *Micrococcus*, *Achromobacter* and *Bacillus* species were used to denitrify the solution in anaerobic conditions, with addition of an organic carbon source. This results in

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formation of nitrogen, carbon dioxide, water and hydroxide. The pH, however, needs to remain approximately neutral and this is achieved by addition of sulfuric acid. The process is highly sensitive to temperature (the reaction rate doubles with a 4-degree increase). Temperatures below 10°C are not advisable for this process.

The HDS process uses ferric sulfate to precipitate ferric arsenate and gypsum. Other metals precipitate as hydroxides during this process. The article by Given and Meyer does not indicate what happened to the precipitates formed in the HDS process, but presumably they are treated as toxic waste.

Cellan *et al.* (1999) carried out laboratory experiments focused on revegetating former mining sites. The high salt content (sodium, nitrate) of neutralized leach material is often a problem. According to Cellan *et al.*, prior leaching of the salts to sufficient depths, with water from local wells, prior to adding a growth medium, yields better results.

White and Schnabel (1998) report that biological treatment was also applied at another Homestake mine, in South Dakota. The paper describes the development and use of a mobile sequencing batch biofilm reactor system. In this case, the organisms were isolated from a municipal waste treatment plant in Fairbanks, Alaska. The authors state that the microbes in their reactor removed all cyanide and, upon addition of glucose, also converted all excess ammonia. The addition of glucose forced the organisms to acquire their nitrogen from ammonia in order to be able to use the glucose. Nitrification and evaporation of ammonia and evaporation of HCN apparently did not take place.

## 7. Examples of cyanide pollution cases

The following example was found on the Internet. Northparkes is an open-pit gold mine in New South Wales that uses cyanide in flotation. When the mine at some point started processing ore with a higher Cu proportion, it probably had to keep adding cyanide to the leach solution. Only the 'free' cyanide contents was monitored in the tailings, and only for process purposes. There was no requirement to monitor WAD. While the measured free cyanide appeared to remain normal, the proportion of copper cyanide complexes in the tailings actually rose and rose which went unnoticed until birds started dying around the tailings dam in May 1995. According to the Australian Minerals and Energy Environment Foundation Australia (AMEEF Australia), copper complexes are especially toxic to birds and 2700 birds died. Measures taken included traditional bird 'scare' tactics that are also used in orchards (AMEEF Australia web site and other sites, listed in references). North regrets the birds' deaths and no longer uses cyanide at Northparkes, according to North Limited's managing director in a press release from September 1996 (North, 1996).

Regretfully, Northparkes recently experienced a disaster of a different nature, when four workers were killed during a cave-in during a shut-down in November of 1999 (Hagopian, 2000 and other sites, listed in references).



The geology of The Netherlands, basically a large river delta, has not yet inspired anyone into starting a gold mine, but the country does have 234 sites of former manufactured-gas plants (Didde, 1995; Meeussen *et al.*, 1994). The first Dutch gas plant opened its doors in 1826 and the last one closed in 1969 (Didde, 1995). In 1995, the total cleanup costs for Dutch former gas plant sites were estimated at NLG 4,000,000,000 (Didde, 1995), which translates into roughly USD 1,600,000,000 at the current high exchange rates. That's a lot of money for a small country tinier than many American counties. The high costs can be attributed to the complexity of the pollutant mix and the location usually being in the middle of residential areas (Didde, 1995).



Fig. 5. A polluted MGP site: the 'Westergasfabriek' in Amsterdam, The Netherlands

A case of cyanide pollution only recently made public is located in Amsterdam, at just a half hour's walk from where I live. The object also photographs conveniently well (Fig. 5). It had been known for years that the grounds of this MGP were seriously polluted, for instance with benzene and heavy metals (EPA). The local belief however appears to be that only a few months ago the pollution was discovered to include cyanide as well.

In 1992, the local city district council acquired the Westergasfabriek (western gas plant), which had closed in 1967. Thirteen of the plant's seventeen structures are pretty and characteristic buildings in neo-renaissance style, with red bricks, stepped gables and other ornaments, built between 1885 and 1905 (EPA). Most of them are now considered national monuments and protected. After cleanup, the terrain will be converted into a park. The buildings already house a cinema, a restaurant, exhibitions, the district's city council, a café, and other facilities and are also home to theater companies, opera performances and conferences. Even the enormous gas tank plays its new role well (Fig. 6).

A local neighborhood paper reported that cyanide was discovered on the grounds in May, after members of a work crew started vomiting and experiencing breathing problems (Landsaat, 2000). A 'strange smell' was reported as well (Landsaat, 2000),



but no further description was given. Members of theater companies rehearsing on the grounds apparently had been complaining about skin rashes and breathing problems for several months (S.J. Reed, pers. comm., 2000), although the significance of this is not clear. According to the health authorities (Milieudienst, pers. comm., 2000), neither is it clear whether the workers actually became unwell due to cyanide poisoning. My personal impression is that the authorities had known about the cyanide contamination, as the opposite would be surprising, but that something, although what is unclear, happened that warranted further action, which included closing off most of the grounds. I have requested but not yet received further information from the authorities about this case. The soils in the lower parts of The Netherlands tend to consist of calcareous clays and have a relatively high pH, while the higher parts have sandy, acidic soils (Meeussen *et al.*, 1994). In view of the location of this MGP site, a sandy soil is unlikely. The groundwater level will be relatively high.



Fig. 6. The remaining gas tank at the Westergasfabriek in Amsterdam is now home to opera performances and conferences.

Performances were canceled, samples were taken, analyses were carried out, and the terrain was cordoned off, according to the local community paper. On July 18, the daily *Het Parool* reported that the local health authorities had declared the situation safe and not compromising the health of residents and visitors.

The information that is readily available appears to be provided by the public and by newspapers (notably *Staatskrant*, 2000), not by the authorities. One of the workers on the Westergasfabriek grounds worried about a red pimple on his chest (Landsaat, 2000). Might it be caused by the cyanide on the terrain? He did not know.

The cleanup approach for Dutch former gas plant sites varies. In the province of Zeeland, 800 truckloads of soil were removed from the Oranjobolwerk site: 10,000 cubic meters of soil were cleaned by extraction and 15,000 were cleaned thermally (Pelgrim, 2000). Another former gas plant site is the Griffpark in Utrecht. The pollution in the Griffpark was discovered in the late 70s. Removing the contaminated soil was considered too costly. Instead, the pollution was isolated by an impermeable clay layer, a concrete wall of about 50 meters deep and 1235 meters long,

and topped by a 1.5 meter thick cap of gravel, a lining, sand and top soil (Marlet, 1999). At Hoogeveen, the authorities removed some 500 truckloads of soil. In addition, more than 2,000,000 cubic meters of groundwater were rid of 187 kg naphthalene, 382 kg cyanide and 97 kg aromatics (Provincie Drenthe, 1997). The Amsterdam western gas plant is on a canal and special attention will need to be given to water pollution. I did notice ducks and coots on the canal, but only a few. The site itself has a lush vegetation, except of course where the soil was recently excavated. According to the Wester gas plant web site and the local neighborhood site, the pollution will be isolated by a steel dam and covered by a layer of 1.5 m of clean soil.



Fig. 7. Grounds behind fences: MGP site in Amsterdam (Westergasfabriek).

According to the Dutch daily *De Volkskrant*, neighboring country Belgium also discovered an interesting case of cyanide pollution two years ago (De Graaf, 1998). Nothing would grow on some spots in the little village of Rumst, where part of the soil was blue. Prussian Blue and high enough cyanide concentrations can result in blue/green soil colors, while ferric thiocyanate complexes may lead to reddish colors (Kjeldsen, 1999). A survey had been carried out once, on those soils with the blue spots where nothing would grow, but no contamination was found at the time. Because nobody had thought of cyanide. Later, a physician pointed out that the blue color might have something to do with iron cyanides. New analyses revealed cyanide concentrations twenty times higher than the Dutch legal limits for soils. Dutch regulation had to be used, because Belgian law did not even mention cyanide. The grounds lie behind fences now but nobody knows who is going to pay for the cleanup. 'The polluter should pay,' said the village's mayor. But who's the polluter? Nobody seems to know. A metallurgical factory once occupied the site, but it is also possible that someone else later dumped wastes on the abandoned terrain. In terms of cleanup, however, nothing much is expected to happen for another ten years. The local community does not appear to be very worried.

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## 8. Conclusions

Cyanide causes problems for mining companies, but there don't seem to be good alternatives for cyanidation yet. If there were, the mining companies would be using them right now, on a large scale. The mining industry and the chemistry profession are highly aware of the problems associated with mining. For example, IUPAC's Chemistry and the Environment Division recently held a workshop in Potchefstroom, South Africa ([http://www.saci.co.za.35th\\_convention.webcirc1.htm](http://www.saci.co.za.35th_convention.webcirc1.htm)), addressing environmental chemistry aspects of mining. South-African chemists appear to agree that Africa's largest pollution problems come from mining (IUPAC, 1999). The public is also increasingly becoming aware of the problems with cyanide. But as this article will have shown, mining is not the only area for which cyanide research is highly relevant. Particularly families with children living close to former MGPs have questions about cyanide as well. The authorities are faced with the difficult task to assess what is tolerable and what is not. There is no clear-cut solution, no straightforward answer. In both kinds of pollution cases, mining and urban, good communication with the public is also vitally important. Dutchmen with pimples should not have to lie awake worrying about cyanide.

Cyanide is an excellent example of a highly interesting research topic that spans a wide range of geochemistry. It also shows geochemistry's relevance for society and the geochemical community's obligation to share its knowledge with society almost too well.

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## Call for proposals EU Geochemical Facility

Applications are invited for access to the EU Geochemical Facility at Bristol University, supported by the European Commission Access to Research Infrastructures action of the IHP Programme. The aim of the Facility is to provide access to modern analytical equipment for research groups who do not otherwise have free use of such equipment in their own country.

The Geochemical Facility contains a number of modern analytical instruments for geochemical studies. These include electron probe microanalysis, ICP-MS, laser ablation ICP-MS, XRF, ICP-AES, XRD Mössbauer (Fe<sup>3+</sup>/Fe<sup>2+</sup>), Fourier Transform Infra-Red spectrometry (CO<sub>2</sub> & H<sub>2</sub>O), LECO (bulk C & S), Nuclear Magnetic Resonance and Scanning Electron Microscopy with qualitative EDS. Analysis of surfaces can be performed using Auger Electron, Secondary Ion Mass and X-Ray Photoelectron Spectrometers. Four well-equipped experimental geochemistry laboratories allow Users to carry out investigations that simulate a wide variety of geological conditions.

Access is restricted to research teams from institutions in EU countries (except UK) plus Bulgaria, the Czech Republic, the Republic of Cyprus, Estonia, Hungary, Iceland, Israel, Latvia, Liechtenstein, Lithuania, Norway, Poland, Romania, Slovakia and Slovenia.

The next deadlines for applications are 15th September and 15th December 2000. Application forms can be downloaded from: <http://eugf.gly.bris.ac.uk> or are available from the address below.

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