



## Ferrates performance in thiocyanates and ammonia degradation in gold mine effluents



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### ABSTRACT

Available technologies for cyanides ( $\text{CN}^-$ ) treatment in gold mine effluents marginally degrade the thiocyanates ( $\text{SCN}^-$ ). Commonly, they convert the  $\text{CN}^-$  into a less toxic compound, such as cyanates ( $\text{OCN}^-$ ), which afterwards are oxidized and generate ammonia nitrogen ( $\text{NH}_3\text{-N}$ ). Thus, the pretreated effluents require additional steps for complete degradation of  $\text{SCN}^-$  and  $\text{NH}_3\text{-N}$ . Recent research shows that ferrates [ $\text{Fe(VI)}$ ] might represent a sustainable option for the efficient treatment of gold mine effluents. In this context, the objective of the present study was to assess the performance of  $\text{Fe(VI)}$  in  $\text{SCN}^-$  and/or  $\text{NH}_3\text{-N}$  treatment, as well as in their by-products degradation. The performance of  $\text{Fe(VI)}$  was evaluated using three different synthetic effluents (solutions) and two gold mine effluents contaminated by  $\text{SCN}^-$  and/or  $\text{NH}_3\text{-N}$ . Results indicated that more than 97% of  $\text{SCN}^-$  were degraded with  $\text{Fe(VI)}$ , while the  $\text{NH}_3\text{-N}$  increased up to 50%, after  $\text{SCN}^-$  oxidation of the presence of  $\text{NH}_3\text{-N}$ , within one hour of reaction time. Consequently, for effluents that contain  $\text{SCN}^-$  and  $\text{NH}_3\text{-N}$ , longer reaction time is required or complementary treatment technologies, such as nitrification – denitrification, should be evaluated for complete degradation of N-compounds.

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## 1. Introduction

Cyanidation process is widely used for the extraction of gold and silver. The high concentrations of cyanides ( $\text{CN}^-$ ) employed for the refractory gold separation, in sulfidic ores, entail the formation of thiocyanates ( $\text{SCN}^-$ ). Although the  $\text{SCN}^-$  are less toxic than  $\text{CN}^-$ , they are more stable and involve a complex degradation path (Logsdon et al., 1999; Budaev et al., 2015). The available technologies for  $\text{CN}^-$  treatment marginally degrade the  $\text{SCN}^-$  and generate toxic by-products, such as ammonia nitrogen (gaseous  $\text{NH}_3\text{-N}$  and/or soluble  $\text{NH}_4^+$ ; Botz et al., 2005; Gould et al., 2012; Oulego et al., 2014). Noteworthy,  $\text{NH}_3\text{-N}$  in mine effluents also originates in explosives. Biological treatment, commonly used for wastewaters, is not suitable for  $\text{NH}_3\text{-N}$  removal in mine effluents, due to high treatment costs and specific conditions of operation, particularly for large flow and cold climate (Jermakka et al., 2015). Hence, additional treatment is necessary for  $\text{SCN}^-$  and/or  $\text{NH}_3\text{-N}$  complete oxidation. In several countries, the  $\text{SCN}^-$  and  $\text{NH}_3\text{-N}$  are subject to

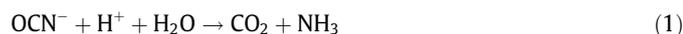
regulation and toxicity testing is required before treated effluents being released into the environment, to protect the receiving waters (Bhunja et al., 2000; Jermakka et al., 2015).

Biological treatment is often the best available technology economically achievable (MEND, 2014), but its range of application is limited to low concentrations of  $\text{CN}^-$  because of the inhibitory effects of several contaminants and temperature on microorganisms' activity (Kuyucak and Akcil, 2013; Villemur et al., 2015). The process involves nitrification [autotrophic oxidation of  $\text{NH}_3\text{-N}$  to nitrates ( $\text{NO}_3^-$ )], and, sometimes, denitrification [heterotrophic reduction of  $\text{NO}_3^-$  to produce gaseous nitrogen ( $\text{N}_2$ )]. For higher concentrations of  $\text{CN}^-$  and  $\text{SCN}^-$ , chemical treatment can be used with the aim of  $\text{CN}^-$  recuperation or chemical oxidation, into less toxic compounds, such as cyanates ( $\text{OCN}^-$ ) and then into  $\text{NH}_3\text{-N}$  (Gould et al., 2012; Kuyucak and Akcil, 2013). The recovery of  $\text{CN}^-$  allows reduction of water loss and the recycling of contaminated effluents. However, the  $\text{SCN}^-$  are not removed and might cause the deterioration of operation units. Partial oxidation into  $\text{CN}^-$  (with recovery and reuse) could be a good option, but only at high  $\text{SCN}^-$  concentrations (e.g., 2000 mg/L) to justify the investment (Adams, 2013; Estay et al., 2013).

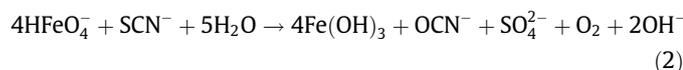
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The oxidation of  $\text{CN}^-$  and/or  $\text{SCN}^-$  into  $\text{OCN}^-$  involve the following processes (Botz et al., 2005; Gould et al., 2012; Kuyucak and Akcil, 2013): alkaline chlorination, ozone, sulfur dioxide and air (INCO:  $\text{SO}_2/\text{air}$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) with Cu(II) as catalyst (Degussa), and peroxymonosulfuric acid (Caro's acid:  $\text{H}_2\text{SO}_5$ ). Alkaline chlorination, commonly used in the past, produced chloramine (as main by-product), which is very persistent in aquatic ecosystems and source of important biohazards (Gould et al., 2012). This technology was replaced by ozone-based process, which is effective for  $\text{CN}^-$  oxidation, but the high cost of an ozone generator limits its use (Kuyucak and Akcil, 2013). The INCO process cannot oxidize the  $\text{SCN}^-$ , which react very slowly under the conditions used for  $\text{CN}^-$  destruction (Gould et al., 2012). Similarly, the Degussa process efficiently oxidizes the  $\text{CN}^-$ , but the  $\text{SCN}^-$  are not removed (Botz et al., 2005). The Caro's acid is very efficient for the treatment of high  $\text{CN}^-$  concentrations. However, it requires high reagent consumption for complete destruction of  $\text{SCN}^-$  (Teixeira et al., 2013). All these processes allow  $\text{CN}^-$  removal, but the generated  $\text{OCN}^-$  are hydrolyzed into  $\text{NH}_3\text{-N}$ , a main source of aquatic toxicity (Eq. (1)). Hence, the gold mine effluents require additional treatments for complete degradation of  $\text{SCN}^-$  and/or  $\text{NH}_3\text{-N}$ .



The advanced oxidation processes (AOPs) are well known for efficiently removing contaminants from water. The AOPs involve the generation of very powerful oxidizing agents, such as non-selective radicals ( $\text{OH}^\cdot$ ), in enough quantities, to enhance the removal efficiency of organic and inorganic contaminants. The AOPs seem an attractive alternative for the degradation of  $\text{SCN}^-$  and  $\text{NH}_3\text{-N}$  in gold mine effluents (Batoeva et al., 2010; Sharma, 2011; Oulego et al., 2014). Among the AOPs, the Fenton-based processes [ $\text{H}_2\text{O}_2$ , with Fe(II) or Fe(III) as catalyst] or peroxydisulfate [ $\text{S}_2\text{O}_8^{2-}$ , in Marshall's acid, with Fe(III)] can transform the  $\text{SCN}^-$  into sulfate ( $\text{SO}_4^{2-}$ ) and free  $\text{CN}^-$ . The  $\text{H}_2\text{O}_2$ , which is a strong but slow oxidant (at low temperatures) is activated by a Fe(II)/Fe(III) catalyst and reacts under acidic conditions (Batoeva et al., 2010; Budaev et al., 2014). Similarly, an accelerated reaction is achieved using the  $\text{S}_2\text{O}_8^{2-}$  radical, which could be activated with the Fe(III) ion, to generate radicals highly reactive in  $\text{SCN}^-$  removal (Budaev et al., 2015). However, the  $\text{NH}_3\text{-N}$  concentrations, when  $\text{SCN}^-$  react with  $\text{H}_2\text{O}_2$  or  $\text{S}_2\text{O}_8^{2-}$ , are very stable, and could increase (Titova et al., 2008). Another strong oxidant used in AOPs is ferrates [Fe(VI)], which are acknowledged as efficient and environmental friendly (Sharma, 2002). The Fe(VI) have been successfully used as oxidants/disinfectants for the treatment of drinking water and wastewater (Jiang et al., 2016; Goodwill et al., 2016). Owing to the fact that the residual Fe(III) generated by the reduction of Fe(VI) is a nontoxic by-product, they are also good coagulants (Sharma et al., 2005; Jiang and Lloyd, 2002). In addition, the Fe(VI) allow the complete oxidation of  $\text{SCN}^-$  and  $\text{NH}_3\text{-N}$  into less toxic degradation products, such as  $\text{OCN}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  as shown in Eqs. (2) and (3).



Thus, the Fe(VI) seems a promising alternative for the efficient treatment of gold mine effluents (Sharma et al., 1998, 2002).

The Fe(VI) are synthesized by electrochemical and chemical processes, which produce either  $\text{K}_2\text{FeO}_4$  [dry Fe(VI)] or  $\text{Na}_2\text{FeO}_4$  [wet Fe(VI)] (Thompson et al., 1951; Alsheyab et al., 2009; Ciampi and Daly, 2009). The dry Fe(VI) are widely used for their long-term stability (Sharma et al., 2005), but their production

involves problems with the separation of the final product, is time consuming and about 12 times more expensive than that of wet Fe(VI) (Waite, 2015). For these reasons, the production of  $\text{Na}_2\text{FeO}_4$  directly on mine sites is likely more advantageous.

Previous studies proved Fe(VI) efficiency in the treatment of gold mine effluents, contaminated either by  $\text{CN}^-$ ,  $\text{SCN}^-$  or  $\text{NH}_3\text{-N}$  (Sharma et al., 1998; Sharma, 2011; Filip et al., 2011; Waite, 2015). However, the performance of wet Fe(VI) in the degradation of  $\text{SCN}^-$  and/or  $\text{NH}_3\text{-N}$  is still little known. In this context, the objectives of the present study were to evaluate the oxidation of  $\text{SCN}^-$  and/or  $\text{NH}_3\text{-N}$  by wet Fe(VI) and to identify/quantify the final products. The knowledge acquired in this study might enable a better evaluation of the applicability of Fe(VI) for the efficient treatment of  $\text{SCN}^-$  and/or  $\text{NH}_3\text{-N}$  in gold mine effluents.

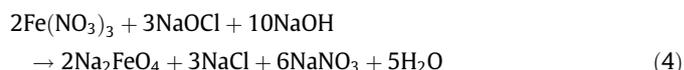
## 2. Materials and methods

### 2.1. Synthetic effluents (solutions) and gold mine effluents

The performance of Fe(VI) was assessed with three synthetic effluents, i.e. solutions (S1, S2, and S3), and two gold mine effluents (E1 and E2), which were sampled on two active sites, at the inlet of the  $\text{CN}^-$  treatment plants (Table 1). Two of the solutions were uni-component and contained either  $\text{NH}_3\text{-N}$  (S1) or  $\text{SCN}^-$  (S2), while the third was bi-component (S3) and contained both  $\text{NH}_3\text{-N}$  and  $\text{SCN}^-$ . The tests carried out with the uni-component solutions were expected to provide information about the independent degradation of  $\text{SCN}^-$  and  $\text{NH}_3\text{-N}$ . The solutions were prepared with ACS grade  $\text{NH}_4\text{Cl}$  and/or  $\text{KSCN}$  dissolved in distilled water. The initial concentrations, which were of  $41 \pm 5$  mg/L  $\text{NH}_3\text{-N}$  and/or of  $120 \pm 2$  mg/L  $\text{SCN}^-$ , are representatives of gold mine effluents.

### 2.2. Synthesis of wet ferrates

The synthesis of wet Fe(VI) (to produce  $\text{Na}_2\text{FeO}_4$ ) was based on oxidation of a Fe(III) salt [ $\text{Fe}(\text{NO}_3)_3$ ] by  $\text{NaOCl}$ , in a strong alkaline solution (i.e.  $\text{pH} \sim 14$ ) of  $\text{NaOH}$ , such as presented in Eq. (4). For this synthesis, 14 g of  $\text{NaOH}$  were dissolved in 50 mL of  $\text{NaOCl}$  (12%), and then 5 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were added in four steps (Thompson et al., 1951; Ciampi and Daly, 2009).



The temperature was maintained at 35 °C, for one hour. The solution was then filtered with a glass filter (Thompson et al., 1951; Jiang and Lloyd, 2002), and the Fe(VI) concentration determined, by UV-vis spectroscopy, using the Beer-Lambert law (Eq. (5)):

**Table 1**  
Composition (mg/L, except for pH) of gold mine effluents E1 and E2.

Parameter	Values	
	E1	E2
$n^\circ$	17	2
pH	$7.5 \pm 1$	$7.9 \pm 0.04$
Eh (mV)	$291 \pm 47$	$431 \pm 34$
$\text{CN}^-$	$19.7 \pm 6.0$	$1.7 \pm 0.3$
$\text{SCN}^-$	$470 \pm 70$	$<0.05^a$
$\text{OCN}^-$	$72.5 \pm 52.5$	$9.0 \pm 1.5^a$
$\text{SO}_4^{2-}$	$2334 \pm 185$	$1013 \pm 54$
$\text{NH}_3\text{-N}$	$62 \pm 18$	$22 \pm 3$
$\text{NO}_2^-$	$2.4 \pm 1.1$	$7.0 \pm 1.5$
$\text{NO}_3^-$	$67 \pm 14$	$37 \pm 10$

<sup>a</sup> As based on the historical data on physicochemical characterization carried out over time.

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