

Oxidation of cyanide in effluents by Caro's Acid

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ABSTRACT

Caro's Acid (peroxymonosulphuric acid: H_2SO_5) is a powerful liquid oxidant made from hydrogen peroxide that has been adopted for the detoxification of effluents containing cyanides in gold extraction plants in recent years.

The present work reports the findings of a study on the kinetics of aqueous cyanide oxidation with Caro's Acid. Experiments were conducted in batch mode using synthetic solutions of free cyanide. The experimental methodology employed involved a sequence of two 2^3 factorial designs using three factors: initial $[\text{CN}^-]$: 100–400 mg/L; $\text{H}_2\text{SO}_5:\text{CN}^-$ molar ratio: 1–1.5–3–4.5; pH: 9–11; each one conducted at one level of Caro's Acid strength which is obtained with the $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ molar ratio used in Caro's Acid preparation of 3:1 and 1:1. The objective was the evaluation of the effect of those factors on the reaction kinetics at room temperature. Statistical analysis showed that the three investigated variables were found to be significant, with the variables which affected the most being the initial $[\text{CN}^-]$ and the $\text{H}_2\text{SO}_5:\text{CN}^-$ molar ratio. The highest reaction rates were obtained for the following conditions: $\text{H}_2\text{SO}_5:\text{CN}^-$ molar ratio = 4.5:1; pH = 9; and Caro's Acid strength produced from the mixture of 3 mol of H_2SO_4 with 1 mol of H_2O_2 . These conditions led to a reduction of $[\text{CN}^-]$ from an initial value of 400 mg/L to $[\text{CN}^-] = 1.0$ mg/L after 10 min of batch reaction time at room temperature. An empirical kinetic model incorporating the weight of the contributions and the interrelation of the relevant process variables has been derived as: $-\text{d}[\text{CN}^-]/\text{dt} = k [\text{CN}^-]^{1.8} [\text{H}_2\text{SO}_5]^{1.1} [\text{H}^+]^{0.06}$, with $k = 3.8 (\pm 2.7) \times 10^{-6}$ L/mg min, at 25 °C.

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1. Introduction

Liquid effluents containing cyanides are generated in some industrial operations such as gold and silver extraction, copper–zinc sulfide flotation, iron making, oil refining and metal–plating. Since most aqueous cyanide species are very toxic, these effluents must be treated before discharge into the environment. Typical legal discharge limits are of the order of 1 mg L^{-1} for total cyanide and 0.2 mg/L for weak acid dissociable complexes (known as WAD cyanide), which include copper and zinc complexes, and free cyanide (HCN and CN^-).

Two methods are employed for the detoxification of effluents containing cyanides in industrial plants: natural degradation and chemical oxidation.

In natural degradation the cyanide-bearing effluents are discharged into a waste pond where they become exposed to the elements. The main natural degradation mechanisms are: volatilization of HCN caused by neutralization to $\text{pH} < 9.3$ of the excess alkalinity by CO_2 absorption from the atmosphere, direct and bio-oxidation of cyanide by dissolved O_2 absorbed from the atmosphere, and solar photolytic decomposition. Natural degradation is a slow process – typically requiring retention times of several days (Smith and Mudder, 1991; Akcil et al., 2003). In most cases the water in the pond will still have $[\text{CN}]$ well above the discharge limits. Gold extraction plants that adhere to the International Cyanide Management Code have to ensure that $[\text{CN}]$ is kept below 50 mg/L , even in ponds that only hold solutions that are recycled (Mudder and Botz, 2004).

Chemical oxidation in cyanide effluent treatment plants at mineral and/or metallurgical plants nowadays employ mainly hydrogen peroxide or a system based on the combination of sulfur dioxide plus air. Alkaline chlorination, a process that was used in the past, is no longer employed. This is mainly because of the formation of by-products (such as chloramines) in the treated effluent that are persistent and toxic to aquatic life, the risk of release of

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toxic and volatile CNCl reaction intermediate, and the significant hazard associated with the handling and storing of chlorine.

Although chemical oxidation carries higher operating costs, it is a much faster, more efficient and reliable way of destroying cyanide when compared with natural degradation. Several plants around the world treat their cyanide effluents through a combination of both processes.

With regard to the kinetics of oxidation, both oxidants mainly employed, hydrogen peroxide and the combination of sulfur dioxide (or metabisulphite) plus air (oxygen), generally perform well. For typical initial [CN] values between 200 and 400 mg/L these processes are reasonably fast (it may take from 30 to 120 min) and efficient (yield of residual CN_{WAD} less than 0.2 mg/L). But with these processes it is essential that the effluent either naturally contains ≥ 20 mg/L of [Cu], or the treatment process includes the addition of a Cu^{2+} soluble salt as oxidation catalyst (usually as concentrated $CuSO_4$ solution), otherwise the oxidation reaction is too slow.

Although cyanide degradation with those oxidants is adequately fast and efficient for various types (compositions) of effluents, there are cases in which a high dosage of the oxidant may be necessary to achieve a higher reaction speed and cyanide removal efficiency level – for example, in the detoxification of slurry effluents (Kitis et al., 2005). In such cases, although it is possible to enhance the oxidation reaction by simply increasing the oxidant dose, other (more powerful) oxidants may be considered in order to attain the legal discharge limits while aiming at minimizing operating costs. In recent years Caro's Acid – peroxymonosulphuric acid (H_2SO_5) – has been used in industry as a more powerful oxidant for the breakdown of cyanides. As with other oxidants, Caro's Acid converts cyanide to cyanate. Cyanate then spontaneously hydrolyses yielding ammonium/ammonia and bicarbonate. As it happens in other cyanide oxidation routes, eventually ammonium may slowly become converted to nitrate in the water through bio-oxidation, and/or simply end up diluted in the water receiving body.

A number still relatively small of gold and silver hydrometallurgical plants already employ Caro's Acid for CN oxidation in effluents; to our knowledge, at least five large scale plants are in operation in South America. For new projects, it is now common to include it in the protocol of experimental trials along with H_2O_2 and SO_2 + air.

The first reports of investigations into the Caro's Acid oxidation of CN in effluents appeared in the early 1990s in the pioneering works published by Smith and Mudder (1991), Nugent and Oliver (1992), Castrantas et al., 1995, Smith and Wilson (2001), Mudder et al. (2001), Botz et al., (2005), and more recently by Breuer et al., 2010. These works describe Caro's Acid oxidation of cyanide and related species in effluents under typical industrial conditions. Nevertheless, we think that it is still relevant to make an addition to the published knowledge on the actual kinetics of Caro's Acid oxidation – in particular, the weight and interrelation of the process variables that can affect the speed and efficiency of reaction – as such knowledge may lead to useful improvements in treatment plant design and the optimization of existing operations.

Thus it has been the objective of the present work to conduct a systematic experimental study on the kinetics of oxidation of aqueous free cyanide with Caro's Acid with a view to attempting to clarify the chemical interrelations of process variables and to build a useful kinetic model. The controlling variables considered at two levels are: initial $[CN^-]$; $H_2SO_5:CN^-$ molar ratio; and pH. Caro's Acid was employed at two strengths (3:1 and 1:1) of $H_2SO_4:H_2O_2$ molar ratio. These control variables, their units and concentration ranges were chosen to correspond to those found by plant, process or design engineers in real cyanide detoxification operations. In such operations the concentration units and the le-

gal limits used for effluent discharge into the environment are mg/L. The pH range of effluents before treatment are limited to pH 9–11, the effluent temperature is normally approximately 25 °C, and there are cost constraints that limit the dose and excess ratios of oxidant to CN^- .

2. Cyanide oxidation with Caro's Acid

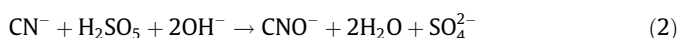
Caro's Acid is a powerful oxidizing agent ($e_H^0 = 1.84$ V). It is prepared by mixing H_2SO_4 (98%) and H_2O_2 (>50%) in a specially designed-for-safety static mixer. The reaction is virtually instantaneous and highly exothermic. The product may reach temperatures as high as 120 °C when starting from reactants at room temperature. As Caro's Acid is unstable at such high temperatures, it cannot be stored as an ordinary chemical. This is an inconvenience for industrial application but was overcome by the development of generators where the reagents are fed in and the hot Caro's Acid produced is immediately cooled and added into the mass of the effluent to be treated.

The following is the equation for the generation of Caro's Acid (Edwards, 1956; Loveitt, 1981):

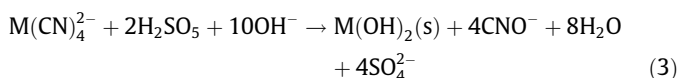


The resulting solution is an equilibrium mixture of H_2SO_5 , H_2O and unconverted H_2SO_4 and H_2O_2 , in which the distribution of these components depend on the molar ratio of reactants (strength) used for the generation of Caro's Acid ($H_2SO_4:H_2O_2$ molar ratio) (Clarke, 1992; Castrantas, 1995).

The oxidation of free cyanide occurs according to the equation:



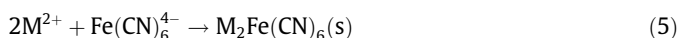
The oxidation of weak metal cyanide complexes occurs similarly; for example, for a divalent metal complex, the equation is:



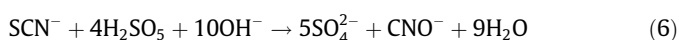
The cyanate produced in the reactions hydrolyses slowly (hours) according to the equation:



If the effluent contains iron cyanide complexes, these are not oxidized. Instead, they may precipitate as an insoluble metal M-iron-cyanide salt, where metal M is usually copper, zinc and/or iron, according to the reaction:



Thiocyanate is also oxidized by Caro's Acid according to the reaction (Smith and Wilson, 1966):



This may be advantageous for improving the removal by precipitating metal ions that may be present in the effluent as the complexing agent SCN^- is eliminated, as well as reducing the residual toxicity of the treated effluent.

As far as speciation goes, it is known (Lente et al., 2009) that H_2SO_5 behaves as a strong acid in its first dissociation step in water, and as a weak acid in the second dissociation step. Thus in mechanistic terms one should bear in mind that the reactant species involved in the redox reaction for the pH range 9–11 will be the conjugated pairs HSO_5^-/SO_5^{2-} ($pK_a = 9.4$) and HCN/CN^- ($pK_a = 9.3$).

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