METHOD FOR REGENERATION OF FREE CYANIDE BY SELECTIVE OXIDATION OF THIOCYANATES

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Abstract:*The invention can be used in the mining industry, the gold mining industry and at non-ferrous metallurgy enterprises for the recovery of free cyanide from waters and pulps containing thiocyanates, as well as for their purification from these compounds. The method includes oxidative treatment of waters or pulps at pH less than 6.0, stripping and trapping of hydrocyanic acid from exhaust gases in an alkaline absorber, alkalization of waters or pulps after their oxidative treatment. Part of the water or pulp after oxidative treatment or stripping of hydrocyanic acid is sent for mixing with the original feed in such a ratio that the pH of the mixture is at the level of 1.5-2.5. Waters or slurries can be treated simultaneously with the recovery of free cyanide to any given depth, and in addition to thiocyanates, cyanides can also be present. Processing is carried out both in periodic and continuous modes, hydrocyanic acid from the exhaust gases is captured by alkaline waters or pulps. The method provides a reduction in the consumption of reagents during the regeneration of free cyanide while maintaining a high degree of their recovery.*

Keywords*:selective oxidation,regeneration, thiocyanates, cyanide,hydrocyanic acid.*

INTRODUCTION

The invention relates to methods for the recovery of free cyanide from waters and pulps containing thiocyanates, as well as their purification from these compounds, and can be used in the mining industry, non-ferrous metallurgy and gold mining.

A known method of purification of wastewater from cyanides and thiocyanates, including the introduction of wastewater into an electrochemical reactor, electrochemical oxidation of thiocyanates at the anode in an acidic environment to obtain hydrocyanic acid and its subsequent neutralization with a solution of hydroxides of alkali or alkaline earth metals. Wastewater is fed into the cathode space, separated from the anolyte by an anion-exchange membrane. Hydrocyanic acid is blown out of the anolyte with air.

The closest in technical essence to the proposed method is a method of regeneration of cyanides by the oxidation of thiocyanates. The method involves contacting thiocyanates in solutions or slurries with a gas containing ozone. The pH value should be in the acidic region, preferably less than 6.0. Under these conditions, cyanide is predominantly in the form of hydrocyanic acid (HCN). Approximately 1.2 kg is required to recover cyanide from

thiocyanates at 90% (theoretical maximum). ozone per 1 kg. thiocyanates. To regenerate free cyanide from hydrocyanic acid, ozone-treated waters are alkalized to a pH of more than 10.0, for example, with lime (CaO). Part of the hydrocyanic acid in the exhaust gases is captured in an alkaline absorber, while cyanides are also regenerated. Exhaust gas can be reused.

The essence of the method is as follows.

Waters or pulps containing thiocyanates are treated with an oxidizing agent in an acidic medium at a pH less than 6.0, preferably 1.5-2.5. As an oxidizing agent, substances or a physicochemical process capable of selectively oxidizing thiocyanates in acidic environments can be used, for example:

1. Oxygen-containing oxidants - ozone, in the form of its mixture with air or oxygen, hydrogen peroxide, percarbonates, peroxides of alkali and alkaline earth metals, etc.;

2. Electrochemical oxidation - electrolysis;

3. Sulfur-containing oxidizing agents - peroxydisulfates containing a group (S_2O_8 2-), etc.

4. In this case, SCN- are selectively oxidized to cyanides, which in turn form hydrocyanic acid. The reaction proceeding in this case is as follows.

5. when using ozone:

$SCN+2O_2+H_2O=CN+SO_4^{2-}+2H^++3/2O_2$ (1)

$CN^-+H^+=HCN$ (2)

6. when using peroxides (hydrogen peroxide):

$3H_2O+SCN^-=H^++SO_4^{2-}+HCN+2H_2O$ (3)

when using electrolytic treatment (electrolysis):

$2SCN^--2e=(SCN)_2$ (4)

$3(SCN)_2+4HOH=HCN+6H^-+HSO_4^-+5SCN^-$ (5)

As can be seen from equations 1-5, during the oxidation of thiocyanates, a hydrogen ion is released, resulting in a decrease in the acidity of the reaction mixture.

The authors found that under these conditions (pH less than 6.0, preferably 1.5-2.5), hydrocyanic acid practically does not react with the above oxidizing agents (i.e., selective oxidation of thiocyanates to hydrocyanic acid occurs), which allows the use of SCN-oxidation products to adjust the pH (to the acidic side) of the process feed without a significant decrease in the specific extraction of HCN. This technique can significantly reduce or completely eliminate the use of acids in the form of a reagent for acidifying the food and increase the degree of regeneration of free cyanide.

The second positive aspect is the possibility of processing waters or pulps initially containing cyanides and thiocyanates. In this case, the cyanides in the initial products pass into hydrocyanic acid and do not participate in oxidative processes.

Hydrocyanic acid formed during the oxidation of thiocyanates in alkaline media recombines into cyanide and water:

$$HCN + OH^- = CN^- + H_2O$$

In this way, the recovery of free cyanide from thiocyanates is achieved.

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