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A THERMOANALYTICAL STUDY OF THE DECOMPOSITION OF A CYANIDE PRECIPITATE IN INERT AND REDUCING ATMOSPHERES

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ABSTRACT

The thermal decomposition of a complex cyanide precipitate from a gold mill effluent treatment process [CANMET acidification–volatilization–reneutralization (AVR) Technology] was studied using thermogravimetry (TG)–Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The precipitate contained KZn cyanoferrates and copper thiocyanate. The TG/FTIR experiments were conducted in He and H_2–He atmospheres. The decomposition was found to occur in three stages. In the first stage, the dehydration of the cyanoferrates and the decomposition of the thiocyanate occurred. In the second stage, the decomposition proceeded with the formation of metallic copper and metal sulphides and cyanides. In the third stage the product contained metallic copper, iron and iron carbide. Iron sulphide was also detected when the decomposition occurred in He alone.

INTRODUCTION

Most gold extraction from ores today is achieved by the cyanidation process. In this process, the ore is leached with dilute cyanide solution to dissolve the gold as $Au[(CN)_2]^-$. The metal is later precipitated from the solution by zinc dust cementation or by adsorption on activated carbon with subsequent caustic elution and electrowinning. In such gold milling operations, a substantial amount of cyanide, in the form of simple and complex base metal cyanides, is lost with the mill effluents. To increase the efficiency and improve the economics of the overall process, an effluent treatment technology has been developed at the Mineral Sciences Laboratories, CANMET, to recover and recycle the cyanide back to the leaching circuit [1]. In this process the waste solution containing cyanide is acidified to volatilize HCN; base metal values (e.g. Cu, Zn, Fe) may also be retrieved as they collect in a residual precipitate.

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In the present work, the thermal behaviour of a metallo-cyanide precipitate from a treated gold mill barren effluent is examined for potential recovery of cyanide species and possibly metal values by pyrometallurgical treatment.

EXPERIMENTAL

Materials and procedure

The starting material was a precipitate obtained by the acidification of a waste barren solution from a Canadian gold leach and recovery operation. A DuPont 9900TA system with a 951TGA module was used in the study. The thermobalance was interfaced with a BOMEM-MB100 Fourier transform infrared (FTIR) spectrometer with a Compaq 386/20e computer capable of simultaneous control of the balance and the spectrometer. In the spectrometer, a 10 cm gas cell with standard KBr windows was used. The evolved-gas transfer line between the thermobalance and the spectrometer was made of small-diameter glass tubing connected to a glass filter for the removal of particulates from the gas stream. The TG and FTIR measurements were made simultaneously.

In the experiments, 20–40 mg samples of the precipitate (dried under ambient conditions) were subjected to programmed heating at 20 °C min^{-1} in a stream of helium or helium–hydrogen mixture with a flow rate of 50 ml min^{-1}.

RESULTS AND DISCUSSION

X-ray diffraction analysis of the starting material indicated the presence of three major components, namely CuSCN, $Zn_3[Fe(CN)_6]_2$ and $K_2Zn_3[Fe(CN)_6]_2 \cdot 9H_2O$, and minor components, possibly $Zn_2[Fe(CN)_6] \cdot 3H_2O$ and unidentified substances. The thermal decomposition of these compounds has been studied previously to various degrees. The decomposition of copper thiocyanate in nitrogen was studied by Batsanov and Zalivina [2] and later by Kabesova et al. [3] using TG, DTA, XRD and IR spectroscopy. They suggested that the decomposition takes place according to the following scheme

$$2CuSCN = Cu_2S(CN)_2 + S \quad 440\,^\circ C,\ N_2 \qquad (1)$$

$$Cu_2S(CN)_2 = Cu_2S + (CN)_2 \quad 645\,^\circ C,\ N_2 \qquad (2)$$

The first reaction was reported to be an exothermic one and the second endothermic [2].

Cola and Valentini [4] studied the decomposition of $Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ up to 300 ° C, and reported that the compound loses the water of hydration but stays stable up to this temperature. The thermal stability of $K_2Zn_3[Fe(CN)_6]_2 \cdot 9H_2O$ also was studied earlier in connection with this material's ultra-high porosity, which compares to that of zeolites [5–7], as well as its desirable ion exchange properties [8]. Most of the studies were done at low temperatures ($< 300\,^\circ C$) using techniques such as thermal analysis, XRD and IR spectroscopy. There is general agreement that, in an inert atmosphere, the material loses its water of crystallization gradually below 250 ° C. Above this temperature, a gradual decomposition of the anhydrous compound occurs with the evolution of cyanogen. In some cases cyanogen was detected in the gas phase throughout the temperature range 200–850 ° C [8].

The thermal decomposition of numerous hexacyanoferrate complexes in nitrogen was studied by Seifer and Makarova [9] using TG, DTA and gas analysis, and also by Chamberlain and Greene [10] using DTA and dynamic gas evolution techniques. The low temperature decomposition of zinc hexacyanoferrate hydrate was studied in a nitrogen atmosphere by Cola and Valentini [4] and in air by Brar et al. [11]. The most comprehensive study of this compound was done by Seifer [12] who concluded that, in an inert atmosphere, $Zn_2[Fe(CN)_6] \cdot H_2O$ loses its water of hydration below 240 ° C. Above 300 ° C, the anhydrous compound decomposes according to the following scheme

$$Zn_2[Fe(CN)_6] = 2Zn(CN)_2 + Fe(CN)_2 \quad 330\,^\circ C,\ N_2 \tag{3}$$

$$Fe(CN)_2 = FeCN_2 + C \quad 450\,^\circ C,\ N_2 \tag{4}$$

$$3FeCN_2 = Fe_3C + 2C + 3N_2 \quad 550\,^\circ C,\ N_2 \tag{5}$$

$$Zn(CN)_2 = Zn + 2C + N_2 \quad 800\,^\circ C,\ N_2 \tag{6}$$

A small amount of cyanogen was detected in the effluent gas at 330 ° C and was related to a slight dissociation of $Fe(CN)_2$ to Fe and $(CN)_2$. Traces of the gas were also detected at 550 ° C but no explanation was given. Above 800 ° C, zinc vapour condensed on the colder parts of the reaction tube. Despite all the published information about the individual compounds, it is anticipated that the decomposition behaviour of the complex cyanide residue may be different.

In the present study, Fig. 1 shows TG diagrams for the cyanide residue in pure helium and in mixtures of 10, 30 and 50% of H_2 in helium. It is apparent that the trend of the weight loss in the different atmospheres was almost the same up to almost 400 ° C. The weight loss at the end of the experiments was also comparable. It is also noticeable that the two diagrams at 30 and 50% of H_2 are almost identical, which indicates that there is no significant influence of hydrogen levels above 30% in the gas mixture on the reaction. The diagrams feature three principal regions. Region 1, the com-

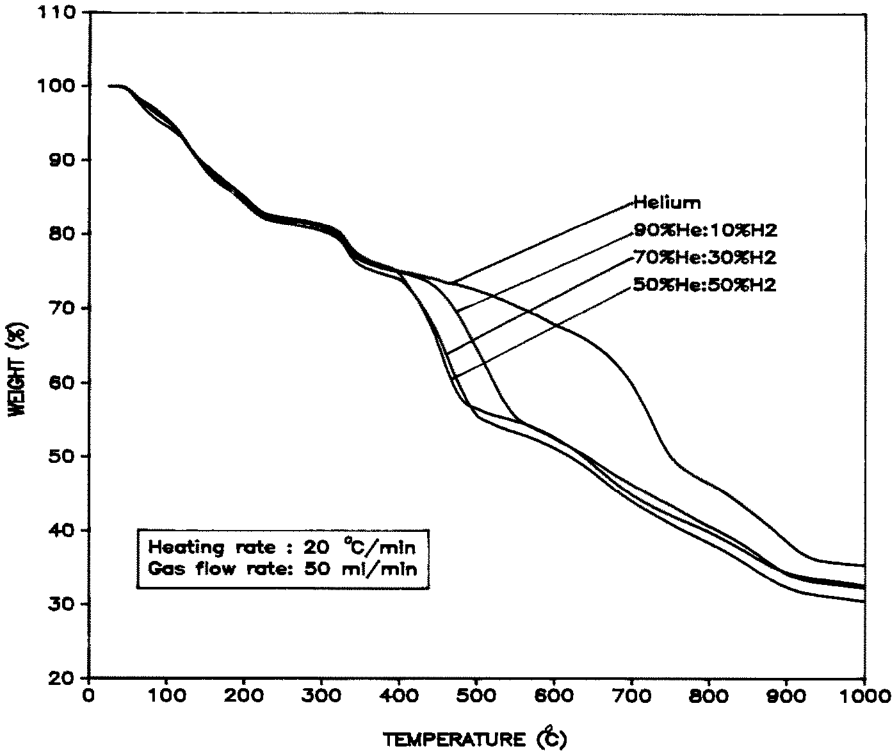

Fig. 1. TG diagrams for the cyanide precipitate in He and He–H_2 mixtures.

mon region, extends between ambient and 350 °C. Region 2 extends from 350–780 °C in the pure helium diagram and to 530 °C in the He–H_2 diagrams, and includes a section of a relatively faster weight loss. This section, which may represent a faster decomposition reaction, appeared at lower temperatures with the increase in the hydrogen content of the gas (up to 30%). This behaviour points to a reaction between hydrogen and a gaseous reaction product, e.g. $(CN)_2$ resulting in a shift in the reaction equilibrium towards a lower temperature. In the case of cyanogen, a reaction such as:

$$H_2 + (CN)_2 = 2HCN \qquad (7)$$

may take place. In region 2, a white deposit that condensed on the colder part of the reaction tube was later identified by scanning electron microscopy (SEM) as elemental sulphur. Region 3 on the diagram contains a gradual weight loss that extends to the ends of the experiments, at 1000 °C. Metallic zinc collected on the reaction tube at high temperature (identified by SEM).

During the course of heating the material, different gaseous effluents were detected by FTIR at different temperatures. Figure 2 shows a re-plot of the TG diagram acquired in pure helium, and the corresponding evolution

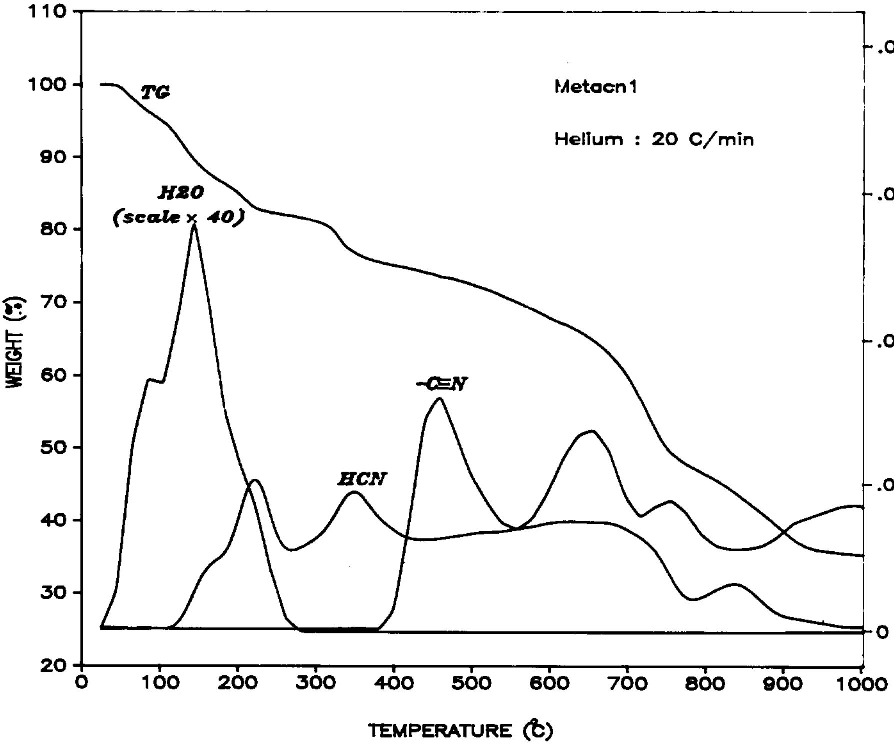

Fig. 2. A TG diagram for the cyanide precipitate in helium with corresponding FTIR gas evolution curves.

profiles for the main gases detected by FTIR. It can be seen that the main species evolved in region 1 is H_2O, which was detected in the temperature range ambient to 150 °C. In addition, a small amount of HCN started to appear above 100 °C and a trace of NH_3 (not shown in Fig. 2) was detected between 200 and 350 °C. In region 2, a nitrile (CN) species [13] started to appear around 380 °C and continued at variable but moderate levels to the end of the experiment. In the same region, CO_2 and later CO (not shown), were detected in the effluent gas and HCN continued to evolve at relatively low levels. In region 3, relatively low levels of the nitrile, CO_2 and CO were detected. Figure 3 shows the spectra of the gaseous species evolved at different temperatures as obtained simultaneously with TG.

The trend of the effluent gas evolution was found to change with the introduction of hydrogen and with the hydrogen content of the gas. This was confirmed by examining the effluent gas profiles in 10%, 30% and 50% H_2 in He and comparing them with the ones obtained in He alone. Figure 4 shows a re-plot of the TG diagram acquired in 70% He–30% H_2 and the corresponding evolved gas profiles. No significant change in the gas profiles was observed in region 1. In region 2, the shift in the fast weight loss step towards a lower temperature was accompanied by a considerable increase in

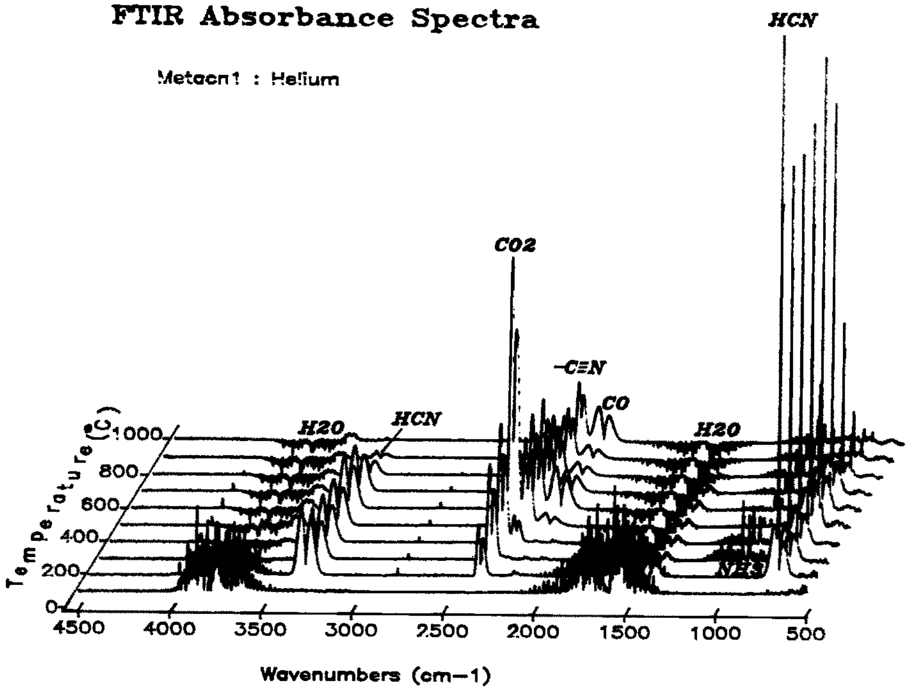

Fig. 3. Absorbance spectra from TG/FTIR of the cyanide precipitate in He.

the amount of HCN and NH_3 and virtual disappearance of the nitrile species at this temperature. There was also a noticeable decrease in the CO_2 and a corresponding increase in the CO content of the gas. In region 3, only CO and nitrile were detected. The effluent gas profiles obtained in 90% He–10% H_2 were found to be intermediate between those obtained in He and in 70% He–30% H_2. The profiles acquired in 50% He–50% H_2 were almost identical to those at 70% He–30% H_2 except for a slight increase in the NH_3 and the elimination of the trace of nitrile. The latter observation confirmed that reaction (7) or a similar reaction had actually taken place.

For further verification of the decomposition route, some experiments were interrupted at selected temperatures and the residues were examined by XRD and in some cases by SEM. It is important to note that, while SEM can detect very small amounts of an element, XRD may not detect components with a concentration of less than 4–5% in the sample. The results are summarized in Table 1.

The results of the XRD/SEM analysis, together with those of TG/FTIR, indicated that, at low temperatures ($< 370\,^\circ C$), the decomposition of the cyanide precipitate proceeded by the dehydration of the cyano complexes and the decomposition of CuSCN. Cyanogen, generated by the latter decomposition, may have reacted immediately with H_2O according to

$$C_2N_2 + H_2O = HCN + NH_3 + CO_2 \qquad (8)$$

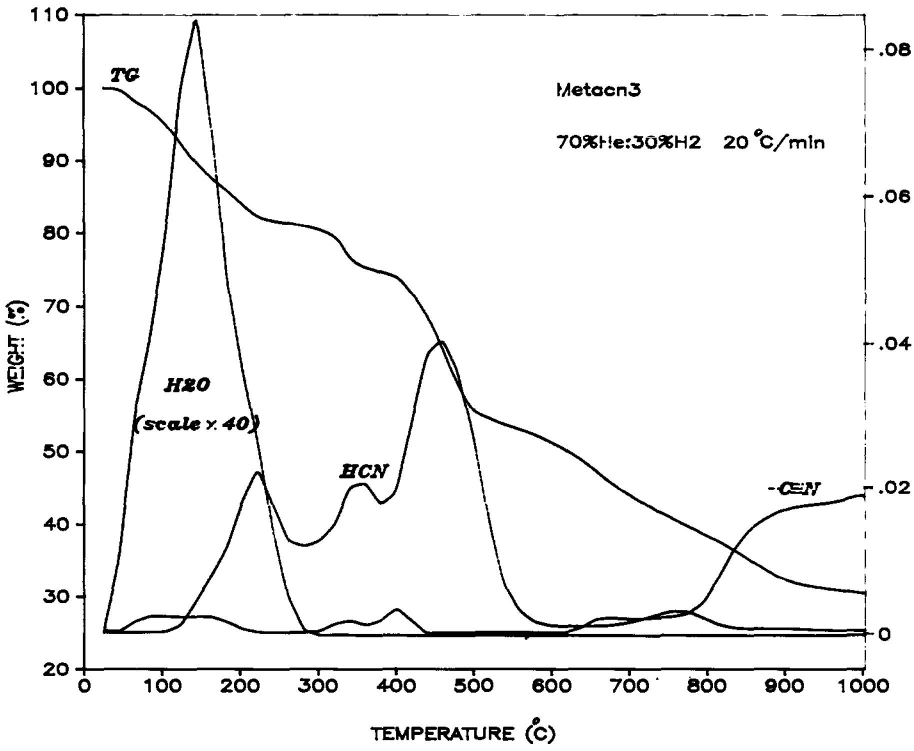

Fig. 4. A TG diagram for the cyanide precipitate in 70% He–30% H_2 with corresponding FTIR gas evolution curves.

which may explain the presence of the three latter gases among the products in this temperature range. At this stage the effect of hydrogen in the atmosphere was minimal. In the temperature ranges 370–780 ° C in He and 370–530 ° C in He–H_2, complete decomposition of the cyano complexes seems to have taken place with the formation of metallic copper, iron and zinc sulphides, and traces of metallic iron. Cyanides of potassium, iron and zinc may also have been present in small amounts. The presence of CO in the intermediate temperature range may be related to the presence of elemental carbon, which reacts with CO_2 to generate CO. At 1000 ° C, in He, the decomposition of all the cyanides occurred and the solid products consisted of metals, iron carbide with some metal sulphides and a complex silicate phase (SEM). In He–H_2 atmospheres, and particularly at high H_2 ratios, Cu and Fe metals, iron carbide, a chalcopyrite-like phase and a complex silicate phase remained in the solid product.

CONCLUSIONS

A complex cyanide product of the above mentioned type, namely a mixture mainly composed of copper, thiocyanate and KZn hexacyanofer-

TABLE 1

XRD and SEM analysis of solids at selected temperatures

Temp. (°C)	Atmosphere	Possible phases by XRD	Elemental analysis by SEM
Ambient	100% He	CuSCN, $Zn_3[Fe(CN)_6]_2$, $K_2Zn_3[Fe(CN)_6]_2 \cdot 9H_2O$, $Zn_2[Fe(CN)_6] \cdot 3H_2O$, *U*	
370	100% He 50% He–50% H_2	$Zn_3[Fe(CN)_6]_2$, $K_2Z_3[Fe(CN)_6]_2$ FeS, ZnS, Cu_8S_5, $Cu_{1.8}S$, $K_2Zn(CN)_4$, *V*	Zn, Fe, Cu, S, K, Ni (trace)
780	100% He	Cu, FeS, ZnS, Fe (trace), *W*	Cu, Fe, Zn, S +S, Fe, Cu, Zn, K
530	50% He–50% H_2	Cu, FeS, ZnS, Fe (trace), *X*	Zn, Fe, Cu, S, K, Ni (trace)
1000	100% He	Cu, Fe, FeC, FeS, *Y*, *Z*	Cu, Fe, S, K +Si, K, Na, Fe [a]
	90% He–10% H_2	Cu, Fe, FeC, *Y*, *Z* (trace)	
	70% He–30% H_2	Cu, Fe, FeC, *Y* (trace), *Z* (trace)	
	50% He–50% H_2	Cu, Fe, FeC, *Y* (trace)	Cu, Fe, S, K +Si, K, Na, Fe [a]

U, V, W, X, Y, Z = unidentified.

[a] complex silicate phase.

rate, decomposes thermally in three main stages. In the first stage, copper sulphide and anhydrous cyano complexes form with the release of H_2O and HCN and small amounts of NH_3, CO_2 and elemental sulphur. In the second stage, the decomposition proceeds with the formation of metallic copper and metal sulphides and cyanides. In the third stage, metallic zinc volatilizes while metallic copper and iron, as well as iron carbide and some sulphides and silicates, remain in the product. In the second and third stages the gaseous effluents may contain some or all of nitrile species, HCN, CO_2, CO and NH_3 in proportions depending on the prevailing atmosphere.

The findings of this study provide more understanding of the behaviour of complex cyanide precipitates during the treatment of gold-mill effluents by CANMETs AVR process for the recovery of cyanide metal values.

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