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FINAL REPORT

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A STUDY OF THE PHOTOCATALYTIC EFFECTS OF AQUEOUS SUSPENSIONS OF PLATINIZED SEMICONDUCTOR MATERIALS ON THE REACTION RATES OF CANDIDATE REDOX REACTIONS

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I. SUMMARY

The proposed research was to systematically investigate the effectiveness of powdered semiconductor materials in photocatalyzing candidate redox reactions. Initially, the rate of the photocatalyzed oxidation of cyanide (CN^-) at platinized TiO_2 was investigated. The extent of the cyanide reaction was followed directly using an electroanalytical method (i.e., Differential Pulse Polarography). Experiments were performed in natural or artificial light.

A comparison was made of kinetic data obtained for photocatalysis at platinized powders with rate data for non-platinized powders.

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II. INTRODUCTION

Numerous solutions are used in the electroplating and other industries that contain high concentrations of cyanide. On occasion, it becomes necessary to discharge these solutions because of contamination or some other problem that renders them ineffective. However, due to the extreme toxicity of free cyanide, it is important to pre-treat these solutions before allowing them to mix into environmental or community water supplies.

Various pre-treatment methods to destroy cyanide are now being applied to industrial waste waters. Many of these involve the addition of some strong ozidizing agent such as chlorine, chromic acid, or potassium permanganate (1,2,3).

By far, the most popular treatment is alkaline chlorination (10). The reactions involved are:

$$CN^- + 2OH^- + Cl_2 \longrightarrow CNO^- + 2Cl^- + H_2O \qquad (1)$$

$$2CNO^- + 4OH^- + 3Cl_2 \rightarrow 2CO_2 + 6Cl^- + N_2 + 2H_2O \qquad (2)$$

These reactions are carried out at a pH above 8.5 with agitation. Complete oxidation of one pound of cyanide requires 8 pounds of chlorine and 7.3 pounds of sodium hydroxide. Although these and other chemicals are effective in destroying cyanide, in many cases their use results in additional volumes of sludge for disposal. Storage and handling of these chemicals present further difficulties.

Electrolytic oxidation of cyanide is also employed as a treatment method (4-9). However, when the concentration of cyanide in the electrolyte falls below 1000 ppm, the rate of the destruction of cyanide decrease significantly. Furthermore, this method requires several hours of electrolysis at high

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current densities (35-100 ASF) and elevated temperature (80-100°C) which may result in the generation and evolution of poisonous hydrocyanic acid.

Rising costs of chemicals and energy present one other major consideration and that is the cost effectiveness of the treatment.

The use of semiconductor materials as electrodes in photoelectrochemical cells has received considerable attention in the past ten years. The principle objective of this research has been to convert solar radiation to either storable fuels (e.g., photoelectrolysis of water to H_2 and O_2) or electrical energy and has been the subject of numerous reviews (see refs. 10-14). A large number of semiconducting materials have been analyzed for their photoreponse characteristics and stability (12,15). In general, the oxides of metals such as $SrTiO_3$ and TiO_2 have been found to be stable in basic solutions but their band-gab limits their response to the UV portion of the solar spectrum.

The extension of the operating concepts of the photoelectrochemical cells to semiconducting powders suspended in electrolytes in order to photocatalyze or photosynthesize chemical reactions has been successful (16,18). The photo-assisted oxidations of a number of compounds including the halogens, CN^- and SO_3^{2-} at semiconducting powders including TiO_2, ZnO, CdS, Fe_2O_3 and WO_3 have been reported (19). A significant enhancement of the oxidation of these compounds has been observed in the presence of e.g., powdered TiO_2 (18,19).

In view of present high costs and other related problems encountered in treating cyanide wastes via "conventional" methods, the development and subsequent implementation of a treatment method employing cheap semiconducting powders and solar energy is desirable. These materials (e.g., TiO_2, ZnO, SnO_2, etc.) are abundantly available at reasonable cost (e.g., \$0.26/TiO_2) and could conceivably be used and reused with only minor preparation.

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The detailed understanding of the kinetics of the photo-induced reactions at the interface between platinized-semiconductor powders and the electrolyte are not yet known. It is, therefore, important that a systematic study be made to determine the effectiveness of these materials in photocatalyzing and photosynthesizing important reactions. A comparison of kinetic data obtained for the photocatalysis of cyanide at platinized semiconducting powders with rate data for non-platinized powders is expected to reveal a significant enhancement of reaction rate.

The Chemistry Department of Southern University-Shreveport has studied the catalytic effects of aqueous suspensions of powdered semiconductor material on the photo-oxidation of cyanide. The purpose of this proposed research was to investigate the effectiveness of powdered semiconducting materials such as TiO_2 and others in photocatalyzing the oxidation of cyanide in industrial waste waters.

III. EXPERIMENTAL

All chemicals used were of reagent grade quality purchased from the following companies: Sargent Welch, J.T. Baker Chemical Company and Alfa, Venton Division. The TiO_2 (325 mesh, 99.9%) was supplied by the Materials Research Corporation and was used without any pre-treatment other than photodepositing platinum.

A. PHOTODEPOSITION OF PLATINUM ON TiO_2

The method employed to photodeposit platinum was as per kroeutter and Bard [20] with some modifications in procedure. A solution of 0.1 M platanic acid (Aldrich Chemical Company) was prepared by dissolving 5.18 grams of $H_2PtCl_6.6H_2O$ in 25 mL of 0.1M HCl. The pH of this solution was first adjusted to 7 with a 0.1M Na_2CO_3 followed by acidification to a pH of 4 with glacial acetic acid. The solution was then placed in a 8.0 cm I.D. petri dish containing approximately 7g of the TiO_2 powder. This suspension contained 2.0g of TiO_2 per 10 mL of solution. The suspension was subsequently carried through several heating cycles

(i.e., heating to dryness followed by volume adjustments with distilled water) on the surface of a hot plate (Model PC-151, Corning). Throughout the heating period, the suspension was magnetically stirred and illuminated with 150W Xenon lamp. The surface temperature of the hot plate was later determined to be 95°C. Platinization of TiO_2 was completed within 8-16 hours.

B. PREPARATION OF CYANIDE SOLUTIONS

A standard working solution of 0.1M CN^- was prepared by dissolving 0.651g KCN in 100 ml of deaerated 0.1M NaOH. The pH of this solution ranged between 12.89 and 13.00. The working solution was diluted with 0.1N NaOH to cyanide concentrations between 0.01M and 0.08M as required. Experiments were conducted in artificial or natural light employing accurately measured aliquots (10-100 ml) of the above cyanide solutions plus 1 gram of semiconductor powder per 10 ml of solution. Artificial radiation was supplied by a 150-W Xenon lamp (Model #6160, Oriel) with all experiments being conducted in a quartz cell to minimize the absorption of UV light. The powder was kept in suspension by bubbling O_2 at a flow of 300 cc/min.

The amount of unreacted cyanide was determined by differential pulse polarography with a PAR Model 384 polarographic analyzer (Princeton Applied Research, Princeton, N.J.) used with a PAR Model 303 static drop mercury electrode. All samples were centrifuged to remove the semiconductor powder and deaerated prior to analysis.

IV. RESULTS AND DISCUSSION

The objective of this research was to determine the efficiency of some platinized semiconductor powder (e.g., TiO_2) on the photocatalysis of cyanide oxidation. The rate of the overall reaction

$$CN^- + O_2 + H_2O \rightarrow CNO^- + H_2O_2$$

was determined under carefully controlled conditions.

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Mixtures of semiconductor powder and cyanide solutions at various concentration levels were permitted to react in the presence of artificial or natural light. Unreacted cyanide was determined by differential pulse polarography. We anticipated that the platinized powders in the presence of light would show significant enhancement of the reaction rate over that for non-platinized powders.

The rate of a photochemical reaction at semiconductor materials depends on various parameters, two of which are the photogeneration of minority (i.e., electrons for n-Type) and majority carriers and the rate at which these are used preventing recombination. In our experiments, oxygen was used as the so called "scavenger" gas for photogenerated holes. For CN^- the process occurred as follows:

$$Pt\text{-}TiO_2 + h\nu \rightarrow Pt\text{-}TiO_2 + 2p^+ + 2e^- \quad (4)$$

$$CN^- + 2OH^- + 2p^+ \rightarrow CNO^- + H_2O \quad (5)$$

$$O_2 + 2e^- + 2H_2O \rightarrow H_2O_2 + 2OH^- \quad (6)$$

The overall reaction is represented in Equation 3.

Figure 1 briefly illustrates the mechanism involved in the oxidation process at the surface of the semiconductor particle. Represented is a single particle of platinized semiconductor powder with platinum sites appearing as shaded areas. The particle might be considered as a short circuited photoelectrochemical cell with the platinum sites serving as photocathodes and the bare powder sites as photoanodes. When light processing the appropriate band-gap energy (~3ev for TiO_2) strikes the suspended particle, electron/hole pairs are photogenerated. Electrons, in n-Type materials, migrate toward the bulk of the particle, eventually finding their way to platinum sites where oxygen is reduced with considerable ease to H_2O_2. The positive holes migrate toward the surface (bare particle/electrolyte interface) where cyanide is oxidized to cyanate (CNO^-). Cyanate is a relatively benign substance which eventually hydrolysis according to Equation 7.

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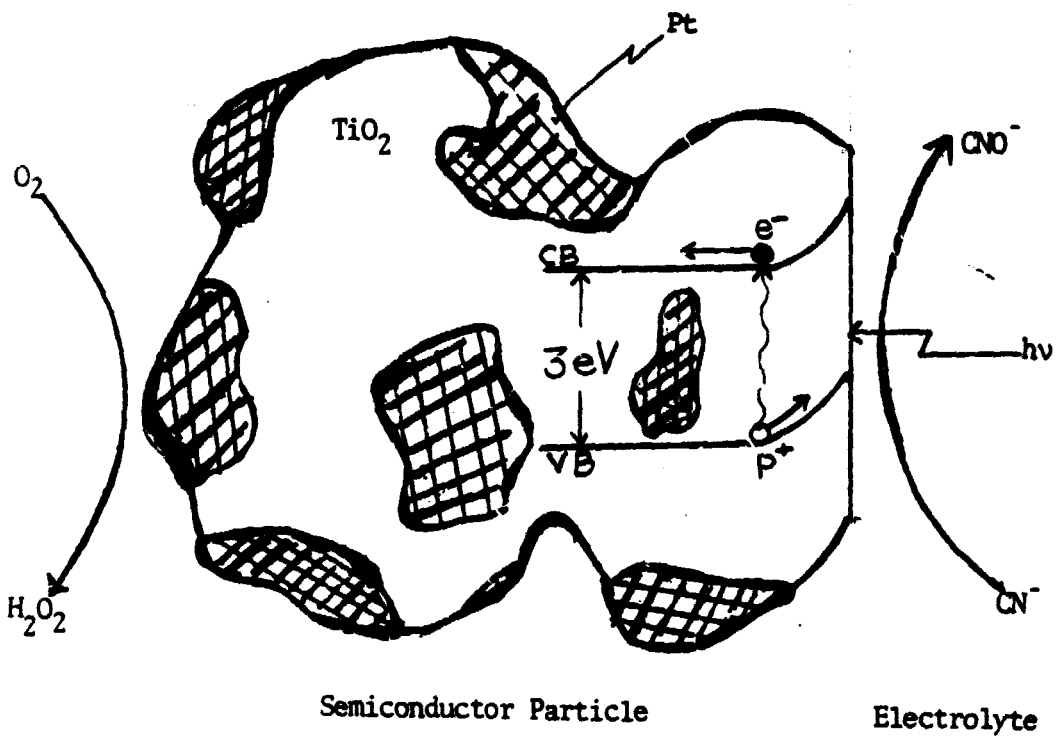

FIGURE 1: Platinized Semiconductor Particle

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$$CNO^- + 2H_2O \rightarrow NH_4^+ + CO_3^{-2} \quad (7)$$

A. ARTIFICIALLY ILLUMINATED SAMPLES

The moles of CN^- reacting with time in artificial light (150W Xenon Lamp) is plotted in Figure 2. As indicated, the amounts of cyanide removed at the platinized powder were significantly higher than at the non-platinized powder. There was a difference of more than 38% for one hour irradiated samples. However, this decreased with increasing in irradiation times (down to 8% for 7 hours irradiated samples).

Table I and II list data used in plotting Figure 2 along with other pertinent information. Column five (5) of each table list the calculated rates at each type of powder. Notice that these show a decrease in reaction rate with irradiation time. Although the slowing in cyanide oxidation is not clearly indicated in Figure 2 for the non-platinized powder, it is somewhat apparent for the platinized powder and is indicated by a break in the curve after six hours of irradiation and at a CN^- concentration of approximately 0.03M.

Figure 3, a plot of reaction rate versus time, further substantiates that the rate of CN^- oxidation at the platinized powder is much higher than at non-platinized powder. Furthermore, it shows a decrease in reaction rate with time for both powders. Previous reports were that the rate of CN^- oxidation at levels between 0.1 mM and .1M is concentration independent, however, this was not the case in these investigations.

Several possible reasons were advanced to explain the decrease in rate with time. Firstly, we suspected that it was due to a decrease in mass transfer efficiency at lower CN^- concentration, thus allowing electron/hole recombination to occur more frequently. However, all solutions were agitated vigorously with O_2 (300 cc/min) during illumination assuring excellent mass transfer conditions.

Secondly, at low CN^- concentrations, the decrease in the rate of oxidation

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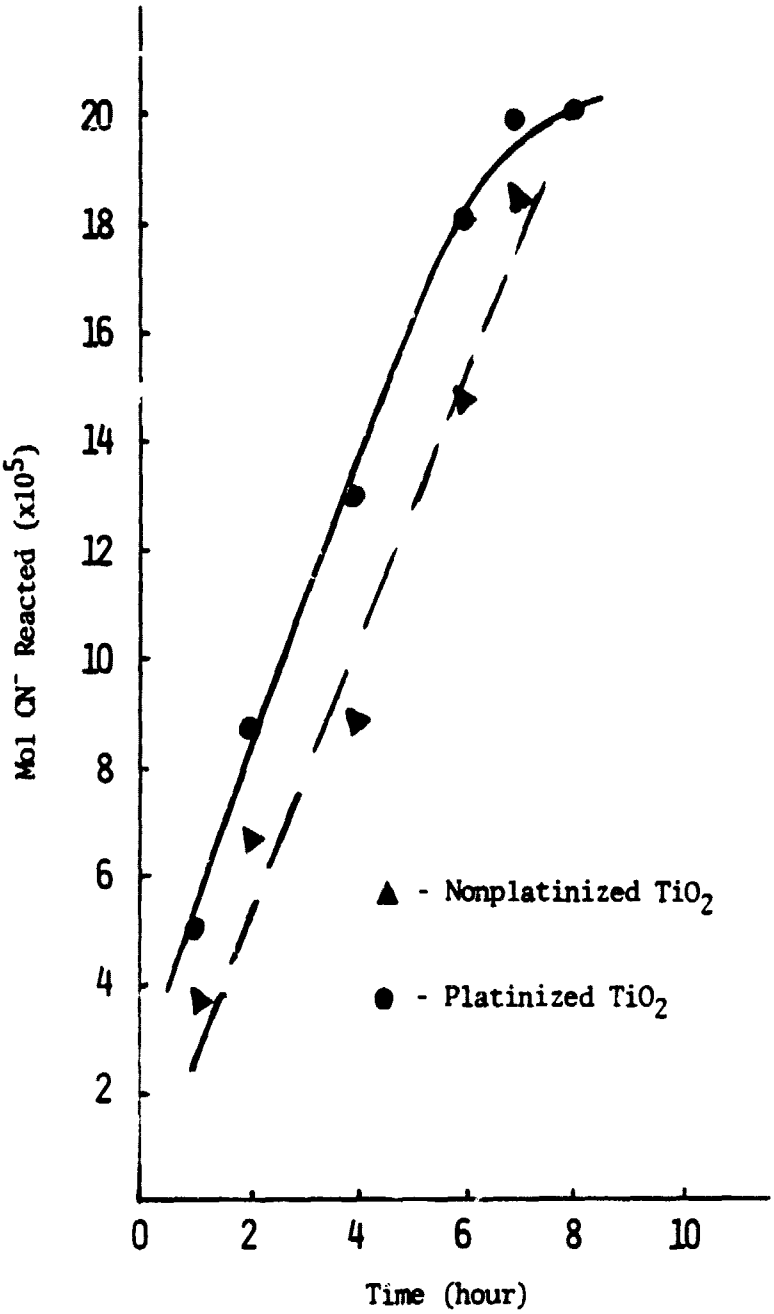

FIGURE 2: Number of mol of CN^- that reacted following irradiation with 150 W Xenon Lamp while bubbling O_2. Solution initially 50 mM CN^- in 0.1 M KOH electrolyte containing 1.0g of semiconducting powder. Solution volume 10 mL.

TABLE I. CYANIDE OXIDATION AT Pt-TiO_2

MOL. $\times 10^{-5}$ INITIAL	FINAL	REACTED	TIME (HOUR)	RATE MOL $SEC^{-1} \times 10^{-9}$
1	2	3	4	5
50.0	45.0	5.0	1.0	13.9
50.0	41.3	8.7	2.0	12.1
50.0	37.0	13.0	4.0	9.0
50.0	32.0	18.0	6.0	8.3
50.0	30.2	19.8	7.0	7.9
50.0	30.0	20.0	8.0	6.9

TABLE II. CYANIDE OXIDATION AT NON-Pt-TiO_2

MOL $\times 10^{-5}$ INITIAL	FINAL	REACTED	TIME (HOUR)	RATE MOL $SEC^{-1} \times 10^{-9}$
1	2	3	4	5
50.0	46.4	3.6	1	10.0
50.0	43.3	6.7	2	9.0
50.0	41.2	8.8	4	6.1
50.0	35.0	15.0	6	6.9
50.0	31.6	18.4	7	7.0

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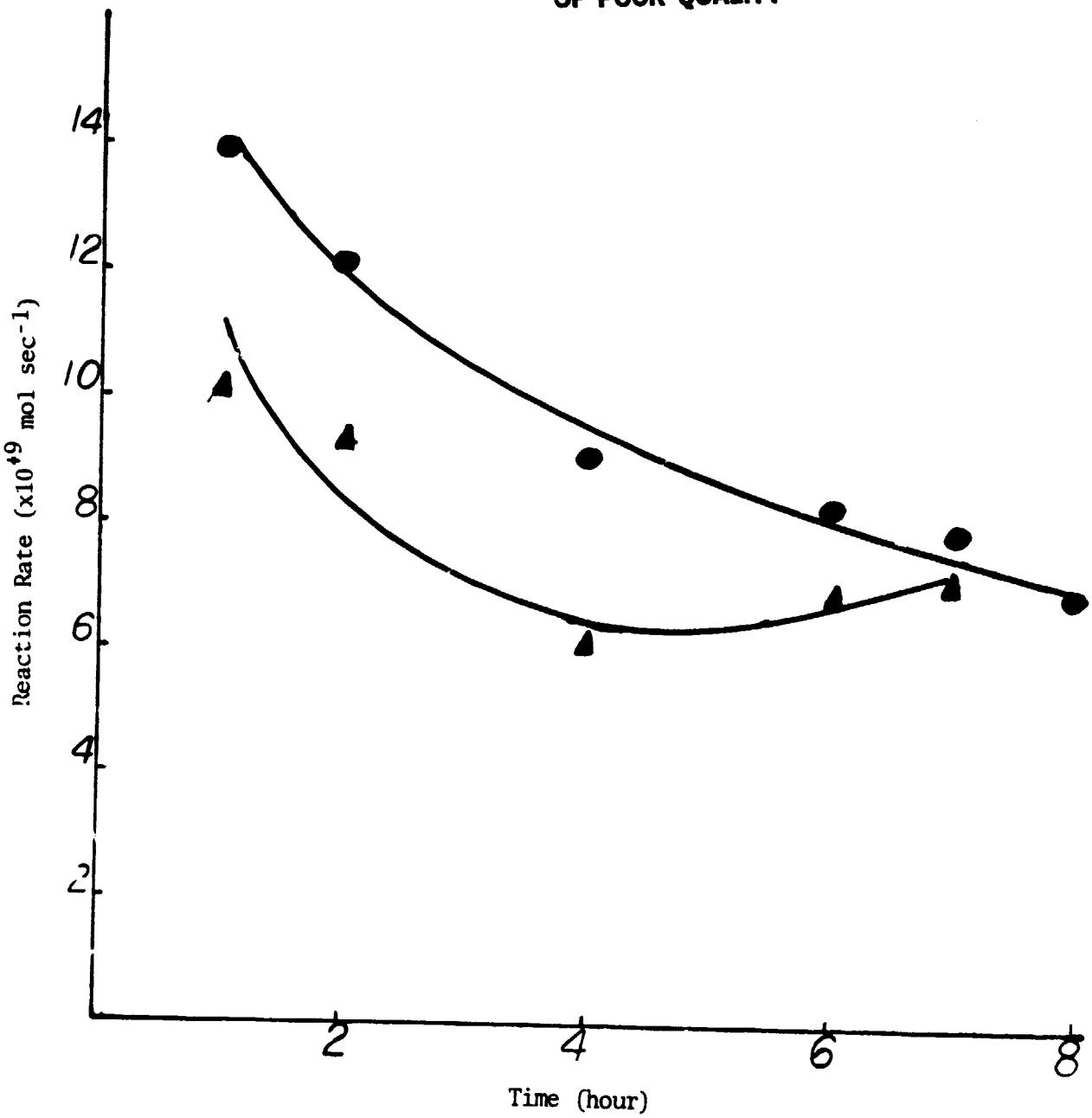

FIGURE 3: Rate of Cyanide Oxidation versus Time

▲ - Nonplatinized TiO_2

● - Platinized TiO_2

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could have resulted from some other electroactive species competing for electron/hole pairs. The concentration of cyanate (CNO^-), product of CN oxidation, increases with time and could possibly compete with CN^- according to Equation 8.

$$2CNO^- + 4OH^- \quad 2CO_2 + N_2 + 2H_2O + 6e^- \qquad (8)$$

resulting in low CN^- oxidation efficiency. Our attempts to investigate this possibility, mandated the development of a reliable analytical procedure for low levels of CNO^-. We selected a spectrophotometric method (21) that involved the formation of a Copper (II)-pyridine - CNO^- complex, the absorbance of which is measured at 480 nm. However, the sensitivity of the method was insufficient and our results were inconclusive.

Finally, the rate might also have been concentration dependent. To examine this possibility, six standard solutions of CN^- (0.01M to 0.06M) were prepared and tested at Pt-TiO_2. Ten milliliters of solution plus 1g of platinized powder were irradiated for two hours with 150W Xenon Lamp. The rate of oxidation was determined for each solution and plotted versus initial concentration of cyanide. The result is shown in Figure 4.

Apparently, the oxidation rate was concentration dependent and increases drastically above 0.03M CN^-.

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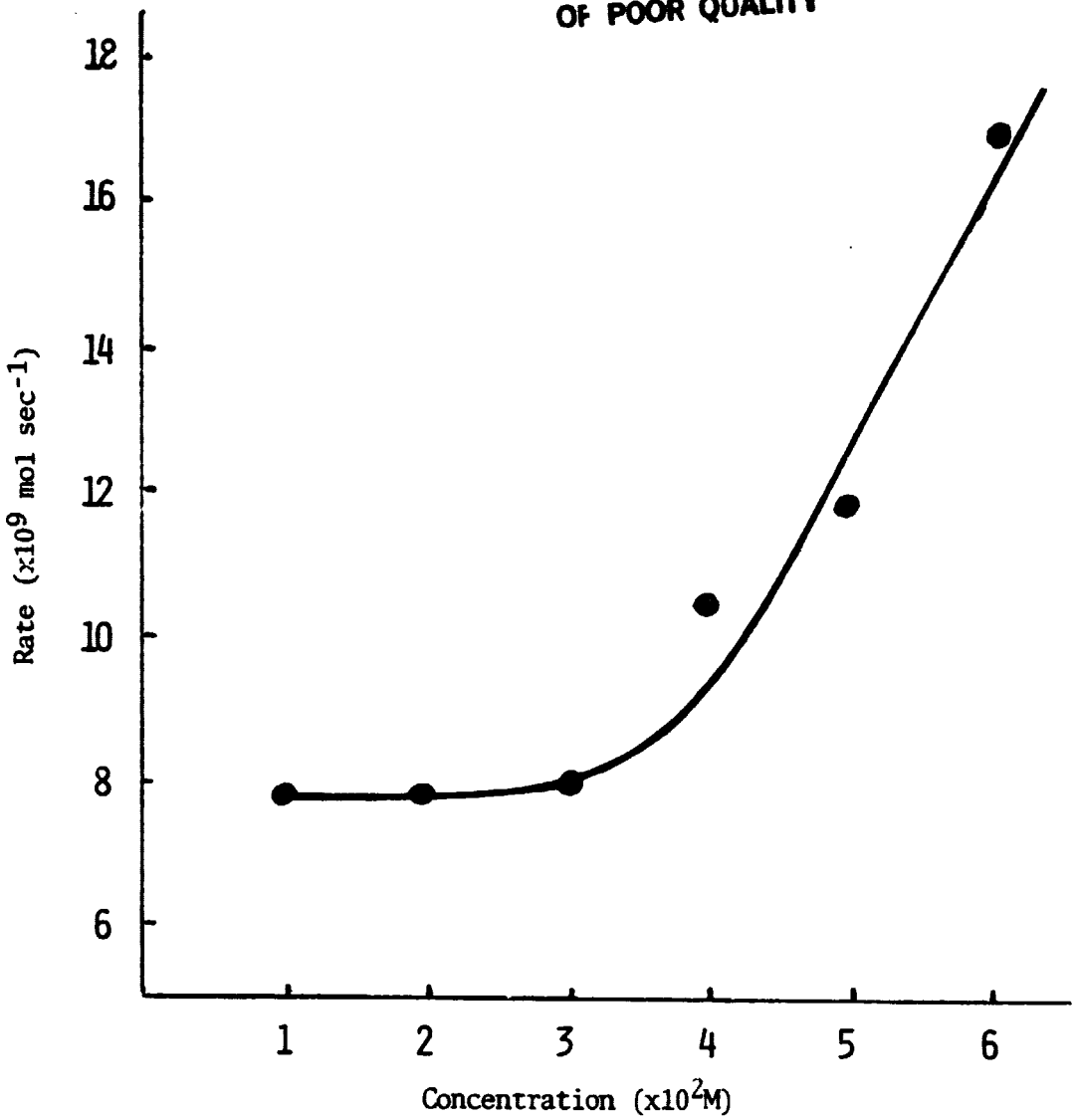

FIGURE 4: Rate of Cyanide Oxidation vs Initial Concentration

Samples contained 1.0g Pt-TiO_2 plus 10 ml of a cyanide solution at one of the concentration indicated. Samples were irradiated with a 150 W Xenon Lamp for 2 hours.

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B. NATURALLY ILLUMINATED SAMPLES

A sample prepared for testing in natural sunlight consisted of 100 ml of 0.05 MCN^- plus 10g of Pt-TiO_2 powder. This mixture was placed in a large petri dish and covered with Saran wrap to prevent volume loss by evaporation. The petri dish was then placed on the roof of a building to maximize exposure to sunlight. A control sample of 100 ml of 0.05 CN^- (No TiO_2) was also prepared and placed along side the test samples.

These experiments were conducted between late April and early May. Weather conditions ranged between heavily overcast to hazily sunlit days with some rain. Temperatures ranged from 4.4°C at night to 80°C at mid-day.

At various time intervals, aliquots were withdrawn and analyzed for cyanide. Table III lists the results obtained which are also plotted in Figure 5.

TABLE III. OXIDATION OF CYANIDE IN SUNLIGHT

DAY	MOL CN^- UNREACTED ($x10^{-5}$)	MOL CN^- REACTED ($x10^{-5}$)
2.0	44.81	5.19
5.0	38.34	11.66
9.0	29.78	20.22
13.0	19.80	30.10
20.0	14.50	35.50
30.0	7.00	43.00

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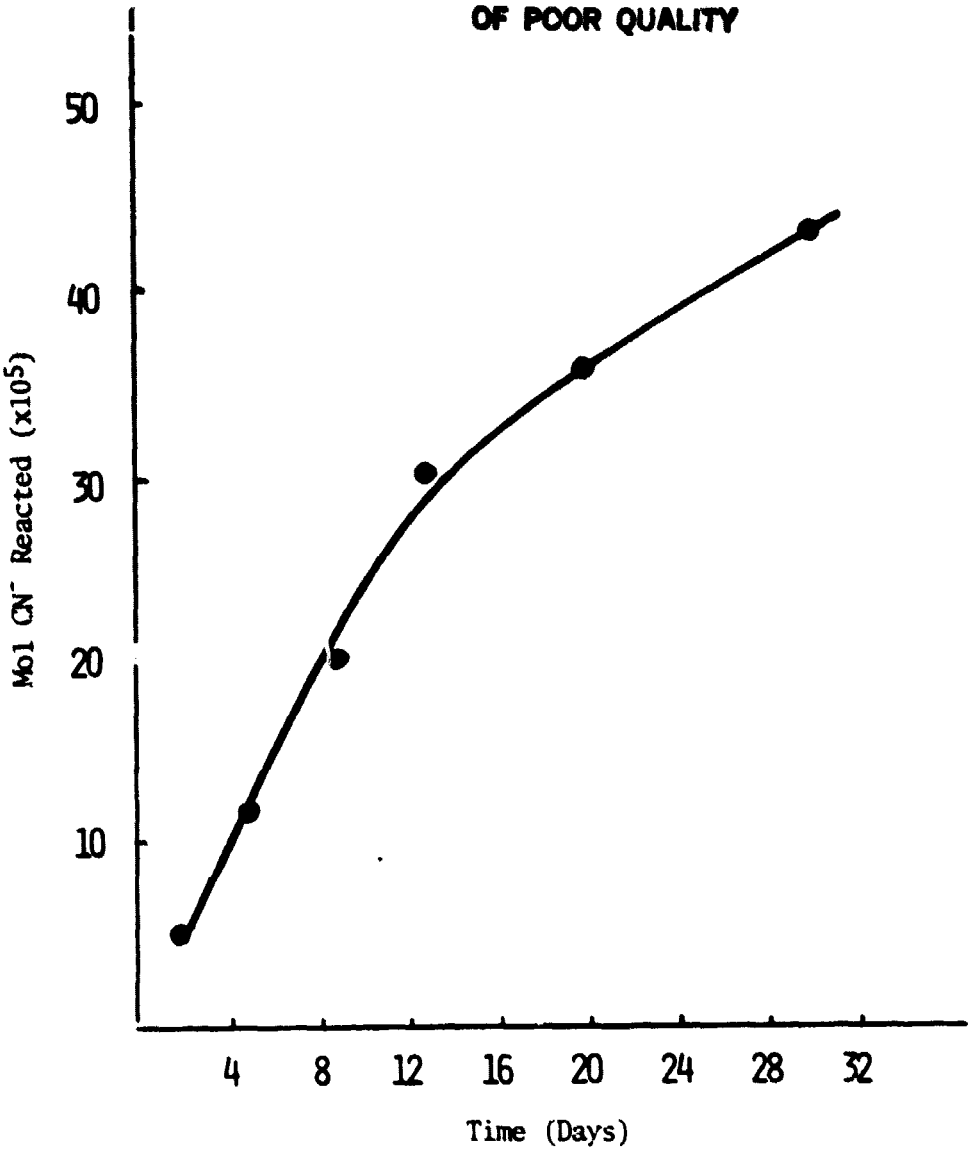

FIGURE 5: Number of Mol of CN^- Reacted vs Time

Number of mol CN^- that reacted in an unstirred solution of 100mL of 50mM CN^- containing 10g of Pt-TiO_2 illuminated with sunlight.

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The rate of oxidation over the first 12 to 13 days was relatively constant. During this period, the concentration of cyanide dropped from 0.05M (1300 ppm) down to 0.03M (780 ppm). Below this concentration level, the reate decreased drastically by as much as 34% of its starting value. Again this seems to indicate a definite concentration dependency of oxidation rate or possible competing electrochemical reactions. Interestingly, the change in rate for naturally illuminated samples occured at approximately the same concentration level as the artificially illuminated samples (i.e., 0.03 CN^-), further substantiating a link between the change in rate with this concentration of cyanide. After 30 days exposure, the concentration dropped to a low of 0.007 (182 ppm).

The oxidation rate for the first 12 days of illumination was determined from least squares fit analysis of both halves of the curve in figure 5. The oxidation rate calculated using the slope, yielded 4.49×10^{-7} mol-day-cm^{-2} of irradiated surface. On the other hand, the rate for the remaining 18 days of testing was 1.51×10^{-7} mol-day-cm^{-2}. The overall rate of oxidation neglecting the two difference rates was 2.85×10^{-7} mol-day-cm^{-2}.

CONCLUSION

A comparison of kinetic data obtained for the photocatalysis of cyanide at platinized semiconductor particles with rate data for non-platinized particles revealed a significant enhancement of reaction rate. Reaction rate at platinized powder (i.e., Pt-TiO_2) increased by as much as 40% in some cases.

Test performed with platinized powder in unfocused sunlight indicated that solutions containing cyanide at levels below 1300 ppm can be effectively detoxified. In fact, solutions with an initial concentration of 0.05M (1300 ppm) CN^- decreased to 0.007M (182 ppm) after 30 days exposure in natural sunlight.

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This procedure could have possible industrial application, however, further tests are warranted on actual industrial wastes samples.

Although important, the information ascertained from this study is relatively limited, therefore, a detailed understanding of photo-induced processes at the interface between platinized-semiconductor powders and the electrolyte still remains a prime objective for future investigations.

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