

# **PHOTOCATALYTIC PROCESS FOR SILVER RECOVERY AND WASH WATER REUSE**

**Illinois Institute of Technology  
Chicago, Illinois**

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## ACRONYMS AND ABBREVIATIONS

ANSI	American National Standards Institute
BTU	British Thermal Unit
cm <sup>2</sup>	centimeter squared
e <sup>-</sup>	electron
ë	frequency and wavelength
E	energy
EDTA	ethylenediaminetetraacetic acid
eV	electron volts
g	gram
hr	hours
Hg	mercury
M	molar
m <sup>2</sup> /g	meter squared per gram
mg/L	milligrams per liter
mL	milliliter
mm	millimeter
mW	milliwatt
N <sub>2</sub>	nitrogen
Nm	nanometer
pH	negative log hydrogen ion concentration
ppb	parts per billion
TiO <sub>2</sub>	Titanium dioxide
UV	ultra violet
v	volt
W	Watt
ZPC	zero point of change
µg	microgram
µm	micrometer

# 1. OVERVIEW

A photocatalytic process incorporating a titanium dioxide ( $\text{TiO}_2$ ) based catalyst can be an effective part of a management program for photoprocessing wash water. The process can rapidly reduce ionic silver to elemental silver, and it can oxidize thiosulfate to sulfate. Removal of silver from dilute wash water will minimize, and possibly eliminate, concerns about potential silver toxicity in wastewater. Furthermore, oxidation of thiosulfate should make it feasible to recycle the wash water.

Following this overview, this report continues with a discussion of the toxicity concerns and economic issues that justify the need for more effective treatment techniques for photoprocessing wash waters. Previous research on similar processes is also reviewed, followed by conclusions and recommendations from this study. The next section contains a description of the experimental methods used to prepare photocatalysts and test their effectiveness at removing silver and thiosulfate from dilute photoprocessing wash waters. We present results from these tests beginning with relatively simple systems to get a better understanding of the process. That information, in turn, is integrated with thermodynamic data and reaction mechanisms to develop a comprehensive picture of reactions in these systems. Subsequent material includes results from studies of catalyst synthesis and evaluation. Following the main body of the report are references and the appendices, which contain data used to prepare the figures.

## 2. THE NEED FOR A COST-EFFECTIVE WASH WATER RECOVERY PROCESS

The photographic industry is the largest consumer of silver in the United States (Cappel et al., 1992). This multifaceted industry includes medical imaging, motion picture, television imaging, and professional and consumer imaging. In each of these imaging applications, silver, a photo-sensitive element, is used to create an image through a series of process steps after the silver is exposed to light. In the process step known as the fix bath, silver is removed from the film as a silver thiosulfate complex. The silver concentration in this fix bath can range from 1,000 - 10,000 milligrams per liter (mg/L) with a typical value of 5,000 mg/L. Currently available electrolytic and metallic recovery technology can be used to recover more than 99 percent of the silver in the fix bath, decreasing the concentration to about 4 mg/L (Dufficy et al., 1993).

Although most of the silver in concentrated photoprocessing solutions is readily recovered, residual silver carried into the subsequent wash baths is largely not recovered. In the wash water, it is much more difficult to recover silver, which occurs as a thiosulfate complex. Silver concentrations in the wash bath generally range from 1 - 10 mg/L. Anion exchange resins are available that can decrease the silver concentration in wash water to 0.1 mg/L or less (Dagon, 1978). Unfortunately, there are numerous potential problems associated with operating ion exchange systems including chronic biological growth, inconsistent process flow stripping silver

from the resin prematurely, and resin fouling (Huang et al., 1996). Furthermore, the cost of an ion exchange system is prohibitive for many small photoprocessing facilities. As a result, application of ion exchange resin technology to recover silver from photoprocessing wash water is very limited (Quinones, 1985; Barbo, 1987). Cappel et al. (1992) estimate the cost of a resin system to recover silver from wash waters ranges from \$15,000 - \$25,000 for a small facility to \$50,000 - \$250,000 for a medium to large facility. Dufficy et al. (1993) believe that requiring the use of this technology for compliance with silver discharge limitations would force 200,000 U.S. facilities to close because of the excessive cost of wash water treatment.

In addition, pretreatment limits with currently available technology are not even achievable in some locations (Table 1). For example, in Reno, Nevada, the local pretreatment silver limit is 0.05 mg/L. Facilities located in this municipality are forced to have photoprocessing wastes drummed and trucked to an area with less restrictive limits. These problems are likely to become more widespread as discharge limits grow more stringent in the face of rising public pressures about the environment (Huang et al., 1996).

Beyond concerns about the potential toxicity of silver released to the environment, there is also a lost opportunity cost when water is discharged. Water is used to wash film accounts for the largest water consumption in a photoprocessing laboratory. For example, the wash water replenishment rate specified for Eastman Color Print Film™ in process ECP-2A is 4.8 liters per 100 feet of 35 millimeter (mm) film. The motion picture industry alone consumes over one trillion feet of print film annually (Morelli, 1997). This film consumption translates to tens of billions of gallons of water used one time to wash the print film processed in only one of many industrial applications that use film.

**Table 1.**—Pretreatment limits for silver discharge to municipal wastewater treatment plants in several U.S. cities.

Location	Silver Limit (mg/L)
Anchorage, AK	0.2
Buffalo, NY	2.0
Los Angeles, CA	5.0
Phoenix, AZ	0.5
Reno, NV	0.05
Riverside, CA	5.0
San Francisco, CA	0.6
San Jose, CA	0.7
Seattle, WA	1.0
Tacoma, WA	0.2

Furthermore, whenever wash water is discharged, energy is wasted. For example, the wash temperature specified in process ECP-2A is 80°F. The cost to heat this water from 40°F to 80°F is substantial. Assuming a national average natural gas price of \$5.00/million BTU (British Thermal Unit), the cost to heat the process water used for motion picture print film is more than \$4 billion annually. Photoprocessing facilities justify this sizable investment because the wash step is critical to the quality and archival keeping properties of the processed film. Washing reduces process solution contamination and improves image stability (Fields, 1976). Problems associated with reducing wash water replenishment rates include loss of image stability and biological growth in the processor, which can affect image quality. An ANSI (American National Standards Institute) Standard for residual thiosulfate on the film governs the measure of a film's archival keeping quality: thoroughly washed film should have a surface residual thiosulfate concentration less than  $1 \mu\text{g}/\text{cm}^2$  (microgram/centimeter squared.) Therefore, silver may be recovered from wash water, but unless the thiosulfate is also removed, the water may not be reused.

In summary, silver is readily recovered from concentrated process solution, but a considerable amount of silver is carried into subsequent wash baths. Although existing ion exchange resin technology can recover silver from the wash water, it is cost prohibitive and typically applied only when local discharge regulations dictate. Cost-effective recovery of silver from wash water and the reuse of the heated process wash water would be welcomed by the photo industry. The only way that this process wash water may be directly reused is to remove both silver and thiosulfate from solution. Previous research suggests that photocatalytic technologies can accomplish these objectives. We review these studies in the next section.

### **3. PREVIOUS WORK ON PHOTOCATALYTIC REDUCTION OF SILVER**

Clark and Vondjidis (1968) conducted some of the first comprehensive studies on the photolysis of silver from silver nitrate solutions. Based on photomicrographs of the system taken at different times, they concluded that silver atoms were able to migrate across the  $\text{TiO}_2$  surface. Apparently, once a silver atom accepted an electron at the surface, that site became a preferential deposition center for additional silver atoms. As a result, reduced silver tended to agglomerate at specific sites on the surface.

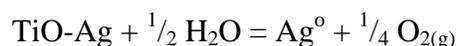
Fleischauer and Shepherd (1974) examined a similar system and also concluded that reduced silver atoms could diffuse across the  $\text{TiO}_2$  surface. In their study, Fleischauer and Shepherd included a reduced iron salt ( $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ ) as another electron donor. They believed that photolytic deposition initially created silver nuclei on the  $\text{TiO}_2$  surface. These nuclei, in turn, became catalytic sites for subsequent redox reactions. An anodic reaction occurred when  $\text{Fe}(\text{II})$  migrated toward the surface and donated an electron. Simultaneously, a cathodic reaction occurred when a silver atom, adsorbed to  $\text{TiO}_2$  at the edge of the nuclei, accepted an electron. The reduced silver atom then diffused to a desirable location in the silver lattice. The authors

thought the electron transfer occurred through the silver cluster because, relative to TiO<sub>2</sub>, silver is a much better conductor. Their conclusions were based on a kinetics argument and supported by electron microscopy. They also reported that the shape of the growing silver deposit varied with the reduction mechanism. Photochemical deposition produced pancake-shaped islands at the surface, whereas Fe(II)-promoted reduction yielded spherical deposits.

Herrmann et al. (1988) reported one of the first applications of this process to a photoprocessing solution. In this case, the products from the reaction were metallic silver and sulfate, indicating that silver was reduced and thiosulfate was oxidized in the process. Silver crystallites can form on the surface from agglomeration of the individual reduced silver atoms (they migrate across the surface). Alternatively, the initial reduced silver atoms can be surface catalysts for subsequent reduction and precipitation reactions.

The authors believed that adsorption was a necessary preliminary step in the photolytic process. They measured maximum silver loading (dark conditions) at 0.44 Ag<sup>+</sup>/nm<sup>2</sup> (nanometer squared) or about 10 percent of the typically reported surface hydroxyl groups.

They observed production of oxygen in their experiments, and their test results were consistent with the following reaction:



Hermann et al. noted, however, that they measured an initial increase in O<sub>2</sub> that was greater than the stoichiometric equivalent. They attributed this excess to the photodesorption of ionosorbed oxygen species (even though they had evacuated the system previously).

In longer-term tests (100-hr) with total silver concentrations up to 0.1 M (molar) they observed no decrease in the reaction rate. Apparently, the silver did not saturate or block the surface.

Although the technology showed promise, they worked with colloidal TiO<sub>2</sub> and it was difficult to separate the catalyst from the solution.

Prairie et al. (1993) further explored the idea that TiO<sub>2</sub> photocatalysis could be used to simultaneously treat waters containing several contaminants. They examined systems contaminated with dissolved metals (Ag, Au, Cd, Cr, Cu, Hg, Ni, and Pt) and a variety of organics (methanol, formic acid, salicylic acid, EDTA (ethylenediaminetetraacetic acid), phenol, and nitrobenzene). From their work, Prairie et al. observed that only those metals with half-reaction standard reduction potentials more positive than 0.3 v (volts) (relative to the normal hydrogen electrode) could be reduced. Furthermore, their data suggest that reduction was proportional to the amount of metal adsorbed to the catalyst. They reported that oxygen inhibited the photocatalytic reduction of silver, mercury, and platinum, probably because of competition for conduction-band electrons. Despite this competition, they felt that oxygen might play an important role in the simultaneous oxidation reaction. The authors concluded that to develop efficient photocatalytic reactions, both reduction and oxidation reactions had to be considered. Finally, Prairie et al. expressed concern that if reduced metals plated onto the

catalyst surface, they might foul the catalyst and limit the process.

In a more recent effort, Prairie and co-workers (Huang et al., 1996) specifically looked at the application of a TiO<sub>2</sub>-based photocatalytic process for the removal of silver from black-and-white photoprocessing waters. (Curiously, they decided not to examine effluent from color processing because they believed it would not transmit UV light). The solutions they tested were spent fixer solutions with silver concentrations ranging from 1,800 mg/L to 6,000 mg/L. They examined the effect of added salicylic acid, EDTA, or citric acid as hole scavengers. There was no effect. It seems likely that there were hole scavengers already present in the fixer solution at higher concentrations.

They also examined the effect of added thiosulfate on the rate of silver reduction. In the absence of thiosulfate, silver was removed to below detectable limits. Removal rates increased with increasing thiosulfate concentrations up through 0.067 M, but higher concentrations resulted in decreased removal rates.

Several observations from this study are especially interesting. Huang et al. (1996) conducted initial tests with a fixer solution that contained about 1,800 mg Ag/L, had a pH between 4 and 4.5, and presumably contained typical, appropriate amounts of sodium thiosulfate, sodium sulfite, and acetic acid. Under these conditions, the TiO<sub>2</sub> surface should have had a positive charge (pH of ZPC of 6.3) and all the silver should have been present as a negatively charged thiosulfate complex. Surprisingly, they reported that under these conditions, the amount of Ag(I) that adsorbed at the TiO<sub>2</sub> surface was negligible when tests were conducted in the dark. Because the surface charge characteristics should have been favorable for adsorption, this observation suggests that, for their catalyst, the surface binding capacity for the silver-thiosulfate complex was relatively small.

The authors also observed an interesting relationship between the amount of silver reduced and the amount of thiosulfate in solution. A test solution prepared with  $1.85 \times 10^{-3}$  M silver (as AgNO<sub>3</sub>) was treated using TiO<sub>2</sub>-based photocatalysis. In the absence of thiosulfate, residual Ag(I) in solution was below 10 ppb (parts per billion) in about 6 minutes. Presumably, water or an organic additive (such as acetic acid) in the fixer was the hole scavenger that was oxidized in the process. Addition of  $6.7 \times 10^{-3}$  M sodium thiosulfate led to an increase in reaction rate, and there may have been an additional slight increase in rate when the thiosulfate concentration was further increased to  $6.7 \times 10^{-2}$  M. However, when the thiosulfate dose was substantially increased to 0.67 M and 6.7 M, reaction rates continually decreased and were less than the rate observed in the absence of thiosulfate. (The last value is unrealistically high; a typical black-and-white process fixer has a thiosulfate concentration of about 1 M). Consistent with these observations and in agreement with the findings reported above from Herrmann et al. (1988), Huang et al. suggested that when added in relatively small amounts, the thiosulfate acted as a hole scavenger and was oxidized to sulfate or sulfite. Apparently, the oxidation reaction was limiting the rate of the overall reaction.

At the higher thiosulfate concentrations, the authors suggested that the inhibition they observed could be caused by the formation of negatively charged silver-thiosulfate complexes that remained stable in solution. To test this hypothesis, they examined the effect of dilution on

reduction efficiency. An initial experiment was conducted with the effluent from an electrolytic process containing 300-ppm silver. Unfortunately, concentrations of other components in this test solution were not given in their paper. Results suggest the composition was different from the typical fixer solutions the authors tested because after 30 minutes of irradiation, they observed no silver removal. Next, the authors diluted the solution with water and reported that silver removal increased with dilution. A 9:1 (water:solution) dilution yielded almost 100-percent silver reduction within 30 minutes. It would be interesting to know how much thiosulfate was present in solution and how much thiosulfate adsorbed to the TiO<sub>2</sub> surface. Without this information it is difficult to understand the mechanisms involved.

Finally, Huang et al. (1996) report that in the systems they studied, the weight of silver-recovered-to-TiO<sub>2</sub> reached as high as 3:1. The authors believed that at these loadings, accumulation of silver on the surface screened the radiation from the catalyst surface, limiting the reaction. At these high loadings, they found that the silver particles were large and weakly bonded to the catalyst surface; they could be removed by sonication.

Interestingly, a potential solution for the separation problem appeared in the literature prior to the work by Herrmann et al. (1988). Kokubu and Yamane (1985) described the preparation of a porous glass-ceramic material, consisting of about 50 percent TiO<sub>2</sub> with surface areas from 100 to 300 m<sup>2</sup>/g (meters squared per gram) and pores as large as 15 nm (nanogram). The authors stated that this material could be prepared in various forms, including a powder, fiber, or plate. Although they felt that their product offered numerous advantages for photocatalytic applications, we are not aware of subsequent work in this area.

In their work on degradation of organic compounds, Low et al. (1991) described an alternative solution to some of the problems associated with working with colloidal TiO<sub>2</sub>. They used a borosilicate glass spiral reactor wound around a 20-W (watt) fluorescent tube. The inner surface of the spiral was coated with a thin layer of titanium dioxide. Although the coating process presumably reduced the effective surface area of the catalyst, they still reported that all the compounds they studied were converted to their inorganic forms. Furthermore, even though this study did not deal with photoprocessing wastes, some of their observations are still relevant to our focus. Specifically, they reported that ammonia, a component of photoprocessing wash waters, could be oxidized to nitrate.

### **3-1. SUMMARY AND RESEARCH QUESTIONS**

Although questions remain about the fate and potential toxicity of silver in the environment, existing and proposed regulations are putting pressure on film processors to remove low levels of silver from their wastewater discharge. In addition to directly addressing toxicity concerns, recovery of silver from wash waters can provide significant economic benefits, including energy savings and water reuse.

Previous studies have shown that a TiO<sub>2</sub>-based photocatalysis can be effective at reducing the silver found in photoprocessing wastewaters. The technology is not likely to become a cost-effective alternative for concentrated solutions such as a fixer bath, which is currently treated using electrolytic recovery or a metallic replacement process. It does, however, hold promise for addressing concerns with dilute wash waters.

Results from previous studies also point to promising areas of development for this technology. For example, the surface properties of the catalyst, including surface area, affinity for the silver species, and conductivity of solid are important, and the catalyst must be prepared in a form that is readily separated from solution. In addition, other species in the solution can be simultaneously oxidized and can play an important role in determining the rate of the overall reaction. The purpose of this study was to begin bringing these concepts together to develop a cost-effective, efficient, reliable, TiO<sub>2</sub>-based photocatalytic reactor for the treatment of dilute photoprocessing wash water.

Based on our review of previous studies, we developed a series of questions to guide this project and continue to evaluate and develop this technology for photoprocessing wash water treatment.

- What are the basic mechanisms of the photolytic process?
- What are the important electron donors and acceptors in these processes?
- What are the dominant forms of silver and thiosulfate in wash water?
- Assuming that a silver-thiosulfate complex dominates silver speciation, does that complex adsorb onto TiO<sub>2</sub>?
- Can complexed silver be reduced, and can complexed thiosulfate be oxidized simultaneously in a suspension of TiO<sub>2</sub>?
- What are the steps in these reactions, and what limits these reactions rates?
- Can answers to the above questions be used to synthesize a more effective catalyst?

Conclusions and recommendations from our study are presented in the next section. Methods used to reach these conclusions are described in the following section.

## **4. CONCLUSIONS AND RECOMMENDATIONS**

A photocatalytic process incorporating a TiO<sub>2</sub>-based catalyst can be an effective part of a management program for photoprocessing wash water. The process can rapidly reduce ionic silver to elemental silver, and it can oxidize thiosulfate to sulfate. Removal of silver from dilute wash water will minimize and, possibly, eliminate concerns about potential silver toxicity in wastewater. Furthermore, oxidation of thiosulfate should make it feasible to recycle the wash water. Specific conclusions include:

- Dominant species in photoprocessing wash water are  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  and  $\text{S}_2\text{O}_3^{2-}$ .
- $\text{Ag}^+$  sorption onto  $\text{TiO}_2$  is typical of cationic metal sorption onto oxide minerals.
- $\text{S}_2\text{O}_3^{2-}$  sorption onto  $\text{TiO}_2$  is negligible.
- $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  sorption onto  $\text{TiO}_2$  is negligible.
- Ionic silver ( $\text{AgNO}_3$  solution) is rapidly reduced when exposed to UV light in a suspension of  $\text{TiO}_2$ . We believe that  $\text{Ag}^+$  adsorbs to the  $\text{TiO}_2$  surface, where direct electron transfer takes place. Surface hydroxyl groups are oxidized in the overall redox reaction.
- Thiosulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_3$  solution) is oxidized when exposed to light in a suspension of  $\text{TiO}_2$ . This reaction occurs even when exposed to fluorescent light. The reaction rate is greater when exposed to UV light. This reaction probably happens indirectly, when hydroxyl radicals released from the  $\text{TiO}_2$  surface oxidize thiosulfate.
- The process works with actual photoprocessing wash water. When a solution containing  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  is exposed to UV light, silver is reduced and  $\text{S}_2\text{O}_3^{2-}$  is oxidized. Hydroxyl radicals released to solution oxidize the thiosulfate, and the released silver adsorbs and is reduced at the surface. The presence of thiosulfate as an electron donor increases the rate of silver removal.
- The composite  $\text{TiO}_2$ - $\text{SiO}_2$  catalyst suggested by Kokubu and Yamane (1985) is not an effective photocatalyst.
- Composite solids synthesized using a sol-gel technique have the potential to be very effective catalysts. Particle size, surface charge, and surface area can be modified to achieve desirable catalyst characteristics.

To continue the development of this process, we recommend the following research in future work:

- Develop a more complete description of the  $\text{TiO}_2$  surface, including the relationship between hydroxyl surface site density and redox active (anodic or cathodic) sites.
- Clarify the fate of the bisulfate buffer that exists in the wash water.
- Examine the fate and clarify the possibility of recovering precipitated silver from the  $\text{TiO}_2$  surface.
- Continue development of customized, sol-gel photocatalysts with surface area and surface charge characteristics that optimize the process.
- Design and develop an efficient, reliable process for field testing and demonstration of the technology.

## 5. TECHNICAL APPROACH

This section includes descriptions of the catalyst preparation and characterization methods, as well as a description of how the photolytic degradation studies were conducted. Unless noted otherwise, reagent grade chemicals were used throughout this study. All labware was detergent-washed, acid-rinsed, and triple-rinsed with double-distilled water.

### 5-1. CATALYST PREPARATION AND CHARACTERIZATION

Numerous reference tests of sorption and photolytic degradation were conducted using Degussa P-25 TiO<sub>2</sub>. This material was used as received, without any pretreatment. Typical properties of Degussa P-25 are summarized in Table 2.

**Table 2.**—Reported properties of Degussa P-25 TiO<sub>2</sub> (Vohra and Davis, 1997).

Characteristic	Values
Crystal structure	80% anatase, 20% rutile
Isoelectric point	5.6 - 6.5
Specific surface area	55 m <sup>2</sup> /g
Surface site density	2.2x10 <sup>-4</sup> to 4.2x10 <sup>-4</sup> mol/g

Turchi and Ollis (1990) reviewed past studies of reactions at the anatase surface and reported that surface hydroxyl site density typically ranged from 7 to 10 OH/nm<sup>2</sup>. Based on the surface area and site density values from Vohra and Davis (1997), spatial density would be from 2 to 4 sites/nm<sup>2</sup>.

An SiO<sub>2</sub>-TiO<sub>2</sub> composite catalyst was prepared following the procedure of Kokubu and Yamane (1985). Briefly, TiO<sub>2</sub> (0.457 mole fraction), SiO<sub>2</sub> (0.526), Al<sub>2</sub>O<sub>3</sub> (0.012), CaO (0.003), and MgO (0.002) were combined and uniformly heated to 200°C for 12 hours. The resulting solid was ground in a mixer mill for 1 hour, and the subsequent powder was used as a catalyst.

A series of catalysts was prepared using a sol-gel technique following procedures described by Anderson and Bard (1995). A TiO<sub>2</sub> sol-gel catalyst was prepared by adding 15 mL (milliliter) of reagent grade titanium isopropoxide drop-by-drop to a beaker containing 250 mL of ethanol and 1 mL of concentrated HCl. Next, deionized water was added dropwise until the solution gelled (typically requiring 15 to 30 mL of water). This gel remained in a covered beaker and aged at room temperature for 1 week. Solvent was then removed in a vacuum oven, and the catalyst was heated to 200°C for 8 hours. The resulting granules were allowed to cool to room temperature and were ground in a mortar prior to testing.

Composite catalysts were prepared by combining titanium isopropoxide with one of the following compounds: aluminum tri-sec butoxide, iron (III) isopropoxide, or magnesium methoxide. At least two versions of each composite catalyst were prepared by combining various proportions of the organic reagents to reach a total volume of 15 mL. Subsequent synthesis steps followed the same procedure as for the TiO<sub>2</sub> sol-gel catalyst.

These synthesized catalysts were characterized using x-ray diffraction, measuring their surface area, and assessing their surface charge through potentiometric titrations. X-ray diffraction studies of these catalysts were conducted using an x-ray diffractometer (Miniflex, USA) using a Cu anode. Surface areas were determined by BET (Coulter SA 3100, USA) analysis of N<sub>2</sub> (Nitrogen) sorption data. The pH of the zero point of charge (ZPC) was estimated by potentiometric titration methods using 300 mL of 10<sup>-1</sup>M, 10<sup>-2</sup>M, or 10<sup>-3</sup>M NaNO<sub>3</sub> solutions that contained 0.2 g (grams) of each sol-gel catalyst. These suspensions were continuously mixed using a magnetic stirrer, and solution pH was adjusted by adding a known volume of 0.1 N HNO<sub>3</sub> or NaOH. The pH value was monitored for 10 minutes and then recorded. This procedure was repeated until the desired final pH value was attained.

## **5-2. SORPTION CHARACTERISTICS**

Batch experiments were used to collect both kinetic and equilibrium sorption data. Tests were conducted both in ambient room light and in darkness. A known mass of catalyst was added to a 500 mL test solution, which was adjusted to the initial desired pH value using 0.1 N HNO<sub>3</sub> or NaOH. For kinetic tests, 20 mL samples were removed periodically, centrifuged to separate the solid and liquid fractions, and the liquid was preserved for subsequent analysis. For equilibrium tests, a 50 mL sample of the suspension was removed, the pH was adjusted, another sample was collected, and this process was repeated until the approximate final pH value was achieved. All of these samples were placed on a tumbling rack for 24 hours, the pH of the suspension was recorded, and then solid and liquid fractions were separated by centrifugation, and the liquid was preserved for subsequent analysis. Total silver concentrations were measured using atomic absorption spectrophotometry (AAS; Perkin-Elmer 1100B). Thiosulfate concentrations were determined using a slightly modified version of Method 4500, a colorimetric titration analytical technique for sulfite described in Standard Methods (APHA et al, 1993).

## **5-3. PHOTOLYTIC DEGRADATION STUDIES**

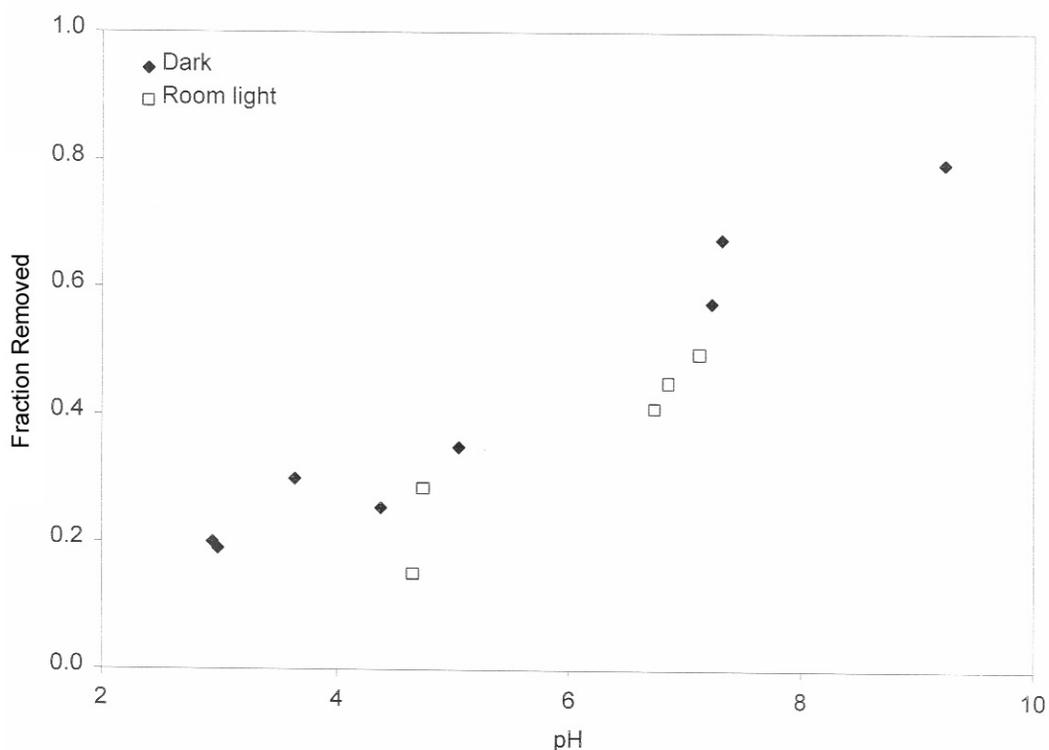
In these studies, a known amount of a test catalyst was added to a 500-mL beaker and maintained in suspension using a magnetic stirrer. A 100-W Hg lamp (Spectroline, with Sylvania par 38 Hg bulb) was fixed 3 cm above the surface of the liquid. Light intensity for this system was periodically determined using a hand-held radiometer (Cole-Parmer Series 9811). Typically, light intensity at the surface of the liquid was about 15 mW (milliwatt) /cm<sup>2</sup>. Solution pH was adjusted by addition of 0.1 N HNO<sub>3</sub> or NaOH. Samples were removed from the suspension at various times, solid and liquid fractions were separated using 0.2-μm (micrometer) filtration or centrifugation, and the liquid was preserved for subsequent analysis. Total silver and total thiosulfate concentrations were determined as noted above.

## 6. INITIAL TESTS: DEGUSSA P-25

This section contains a description of the results from sorption and photolysis tests using Degussa P-25 as the photocatalyst.

### 6-1. SORPTION

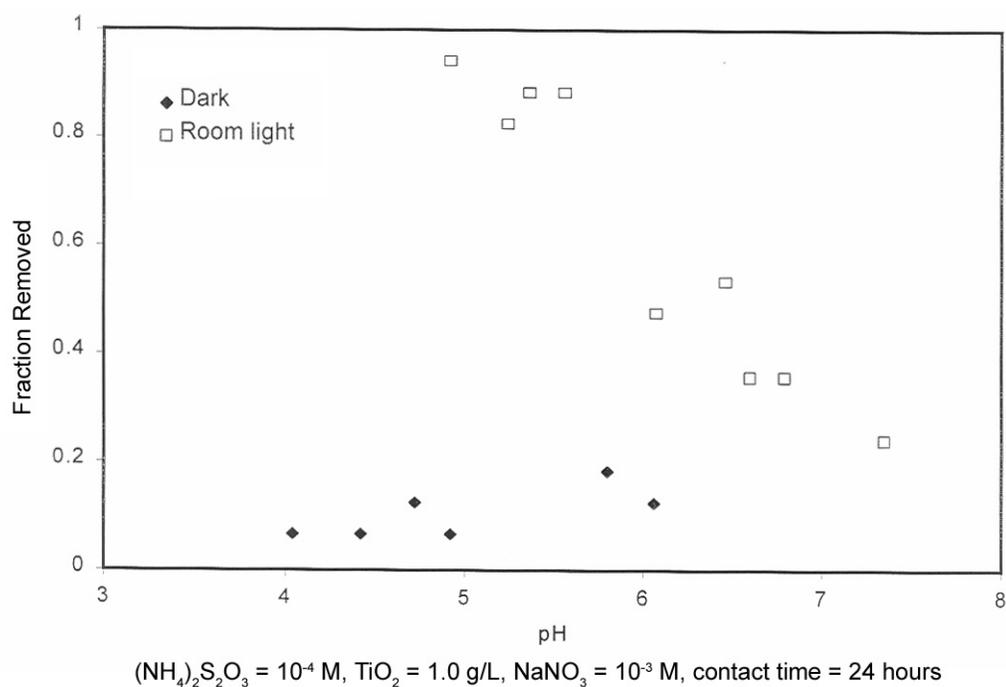
In the pH range of interest, the dominant silver species in a dilute  $\text{AgNO}_3$  solution is the free metal cation,  $\text{Ag}^+$ . The adsorption edge (Figure 1) is typical of metal cations; removal onto the  $\text{TiO}_2$  surface increases with increasing pH. Furthermore, test results indicate that there is no apparent difference in behavior between ambient room light (fluorescent tubes) and darkness.



Silver added as  $\text{AgNO}_3$  ( $\text{Ag} = 2.0 \text{ mg/L}$ ),  $\text{TiO}_2 = 0.5 \text{ g/L}$ ,  $\text{NaN}_3 = 0.01 \text{ M}$ , contact time = 24 hours.

**Figure 1.**—Silver fractional removal onto Degussa P-25.

Similar tests were also conducted with a dilute solution of ammonium thiosulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_3$ ). In contrast with the behavior of silver, the thiosulfate sorption edge (Figure 2) shows that there is a difference between darkness and ambient room light. Uptake by sorption alone (tests conducted in the dark) is only about 10 percent of the total. However, when the same test is conducted under fluorescent light, solution concentration is a function of pH. Interestingly, these results show decreasing removal with increasing pH, which is a typical result for sorption of oxyanions (such as phosphate or selenate) onto oxide solids. In the present case, however, removal from solution depends on the presence of light.

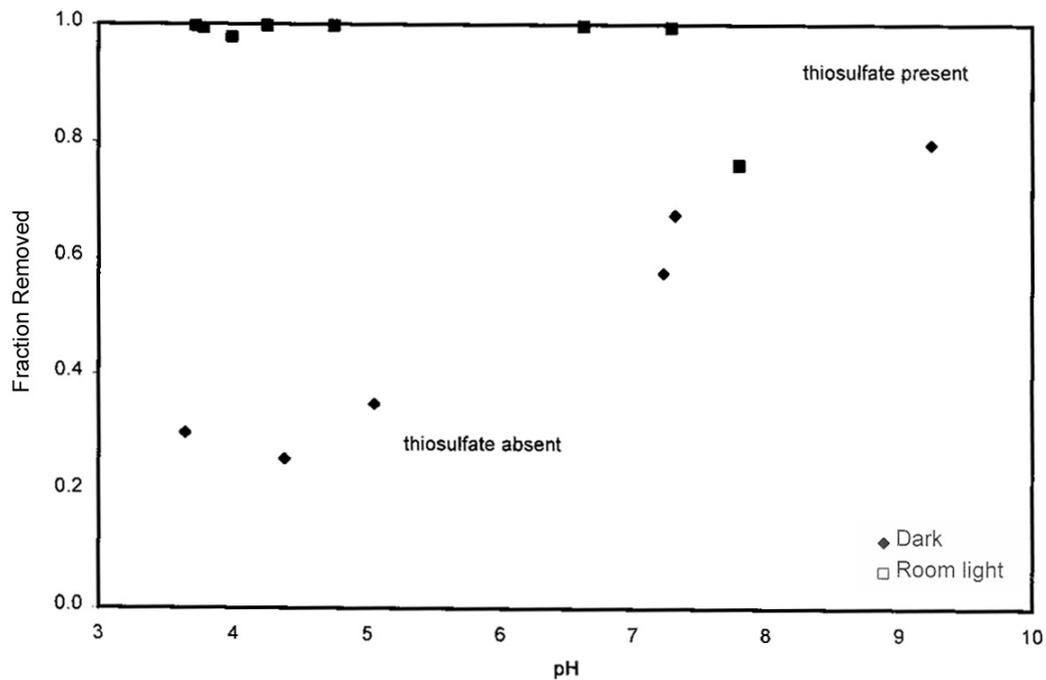


**Figure 2.**—Thiosulfate fractional removal onto Degussa P-25.

These relatively simple solutions may not reflect the behavior of the target compounds in actual photoprocessing wash waters. For example, the presence of thiosulfate has a dramatic effect on silver uptake onto TiO<sub>2</sub> (Figure 3); removal is significantly enhanced, especially at lower pH values. Similarly, uptake of thiosulfate by TiO<sub>2</sub>, which increases from darkness to room light, increases even more when silver is present in solution (Figure 4).

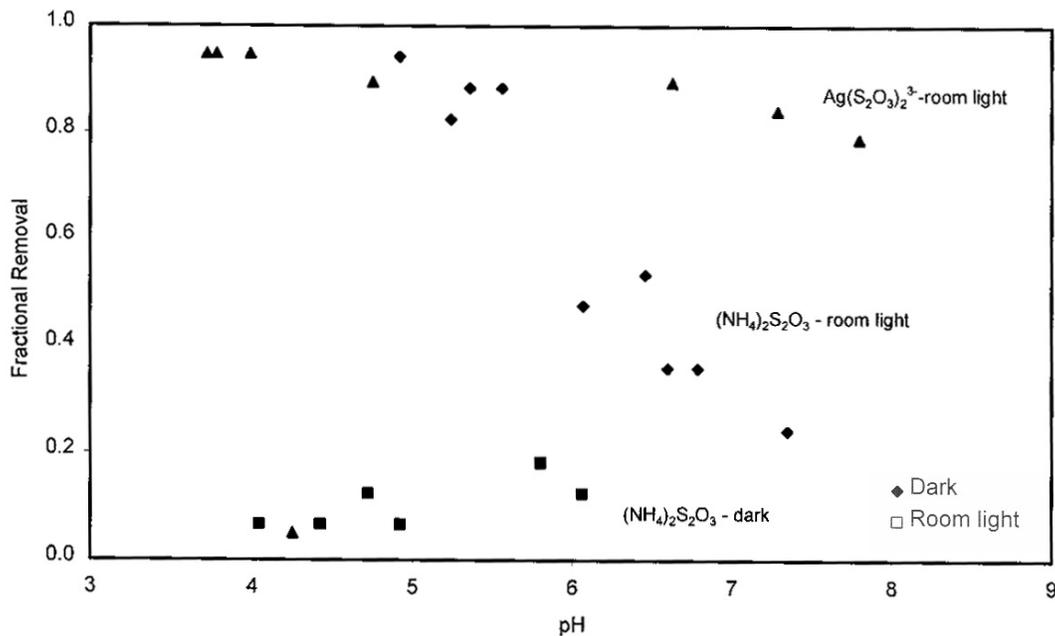
## 6-2. SORPTION RESULTS SUMMARY

These tests suggest that silver or thiosulfate behavior in a suspension of TiO<sub>2</sub> depends on the bulk solution composition. As a free metal cation, silver uptake onto TiO<sub>2</sub> is similar to that of other cationic metals; it increases with increasing pH. Surprisingly, silver removal is enhanced when thiosulfate is present. Most of the silver should be complexed by thiosulfate; our results suggest that the complex adsorbs in a ligand-like fashion. Thiosulfate removal onto TiO<sub>2</sub> is negligible in the dark, enhanced in fluorescent lighting, and further enhanced when silver is present.



Without thiosulfate:  $AG_T = 2.0 \text{ mg/L}$ ,  $TiO_2 = 0.5 \text{ g/L}$ ,  $NaNO_3 = 0.01 \text{ M}$ .  
 Without thiosulfate:  $AG_T = 10.8 \text{ mg/L}$ ,  $TiO_2 = 1.0 \text{ g/L}$ ,  $NaNO_3 = 10^{-4} \text{ M}$ ,  $SO_{3,T} = 1.27 \times 10^{-5} \text{ M}$ .

**Figure 3.**—Influence of thiosulfate on silver removal onto Degussa P-25.



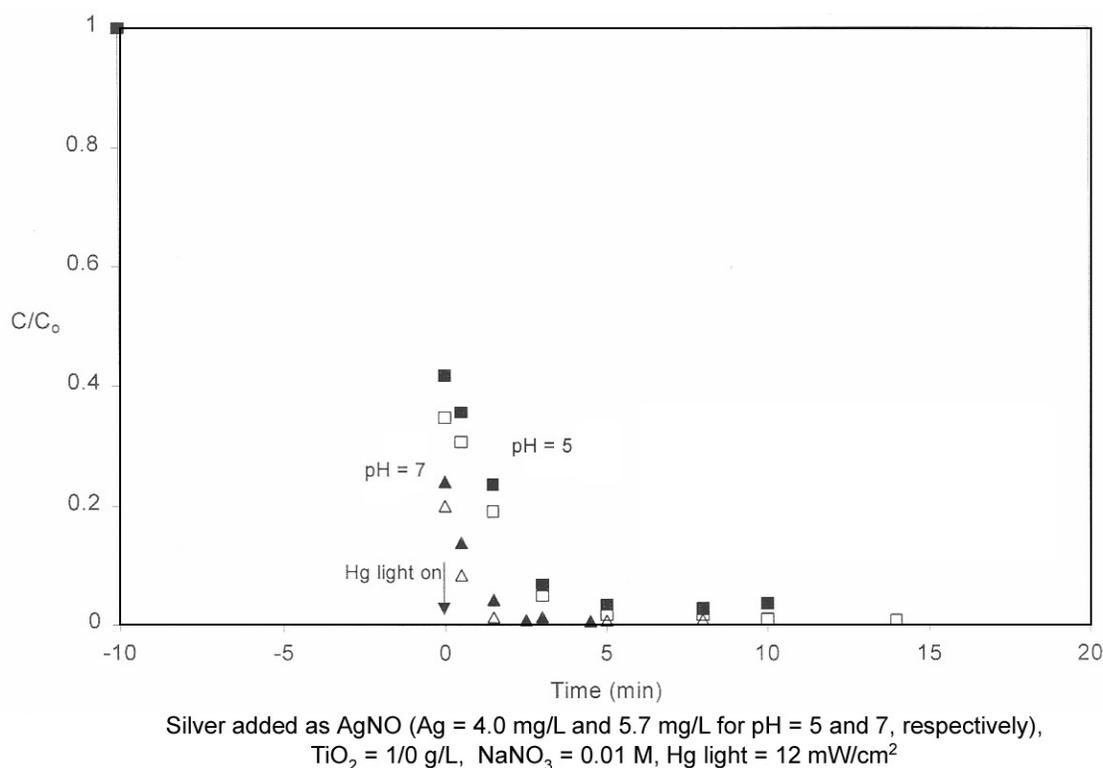
$(NH_4)_2S_2O_3 = 10^{-4} \text{ M}$ ,  $TiO_2 = 1.0 \text{ g/L}$ ,  $NaNO_3 = 10^{-3} \text{ M}$ ,  $Ag_T = 10.8 \text{ mg/L}$ , contact time = 24 hours.

**Figure 4.**—Influence of light or silver on thiosulfate fractional removal onto Degussa P-25.

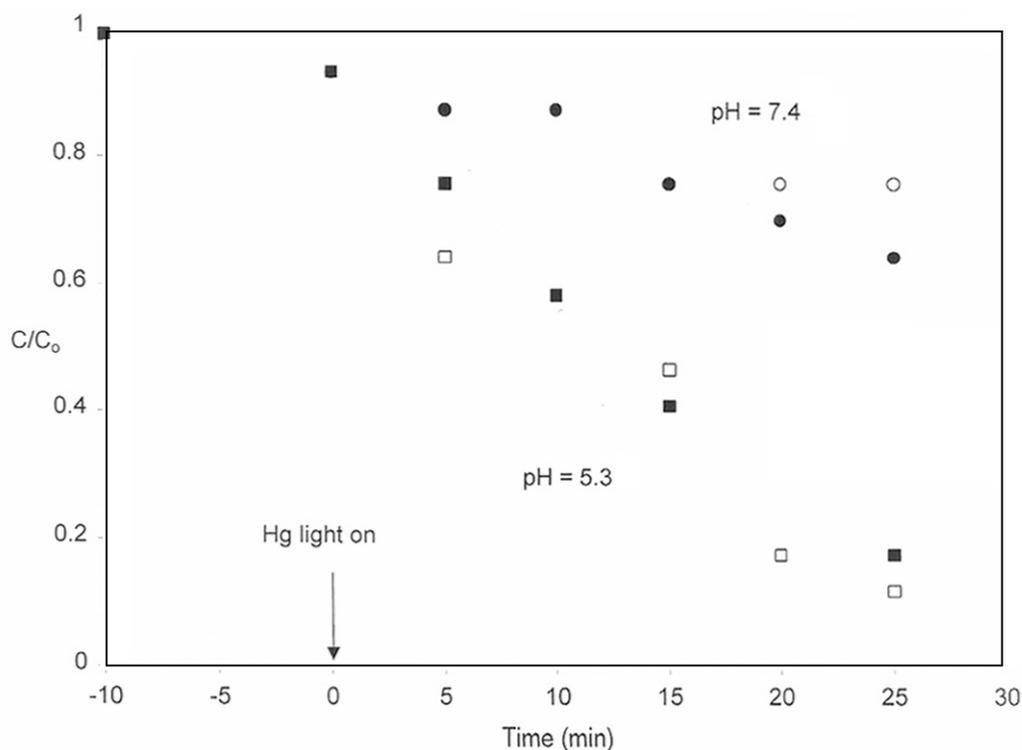
### 6-3. PHOTOLYSIS

In the presence of a UV light source, silver removal from solution continues beyond what can be attributed to sorption alone (Figure 5). Although we did not confirm the presence of reduced, metallic silver in our system, our results are in agreement with previous studies of the photolytic reduction of silver by  $\text{TiO}_2$  (Fleischauer and Shepherd, 1974; Hermann, et al., 1988; Prairie et al., 1993; Huang et al., 1996). Additional tests comparing silver removal at  $\text{pH} = 5$  and  $\text{pH} = 7$  demonstrate that even though sorption (and possibly the initial photolytic reaction rate) is less at a lower  $\text{pH}$  value, once the UV light is on, silver is rapidly removed from solution even at the lower  $\text{pH}$ .

In similar tests conducted with a UV light source, total thiosulfate concentration decreases after the light is turned on (Figure 6). Whereas the photolytic reactions with silver appeared to be complete within 10 minutes, these reactions with thiosulfate continue for at least 30 minutes. Solution  $\text{pH}$  is also important. After 25 minutes, fractional removals are about 90 percent and 30 percent for  $\text{pH} = 5.3$  and  $\text{pH} = 7.4$ , respectively.



**Figure 5.** —Kinetics of silver removal at  $\text{pH} = 5$  or  $7$  in a suspension of  $\text{TiO}_2$ .



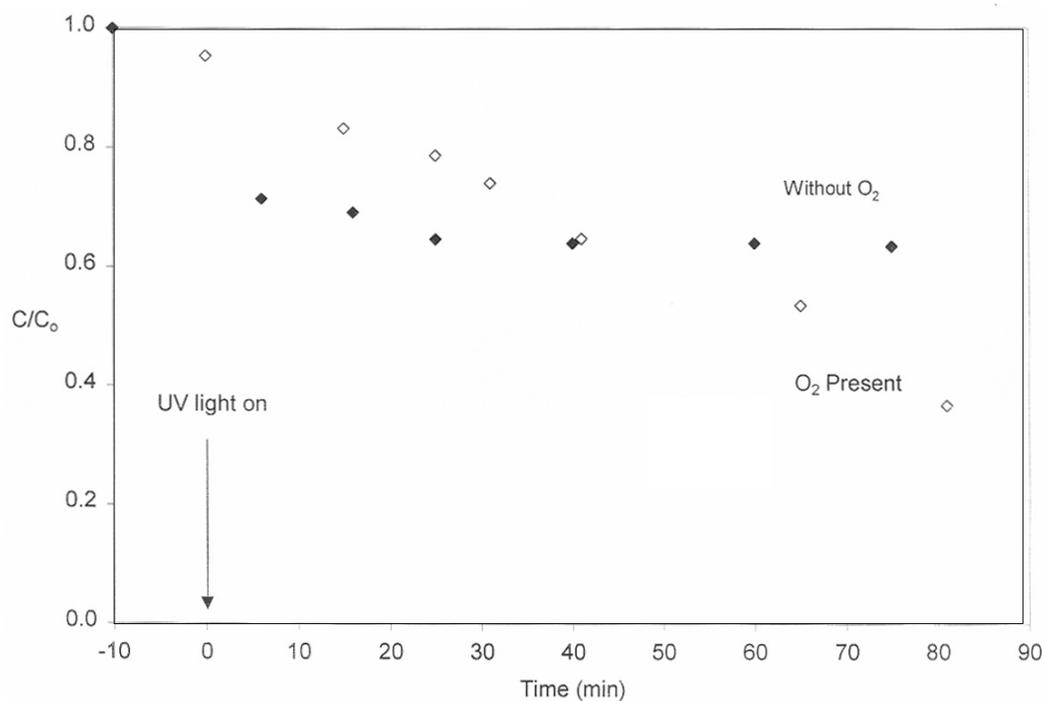
$(\text{NH}_4)_2\text{S}_2\text{O}_3 = 10^{-4} \text{ M}$ ,  $\text{TiO}_2 = 1.0 \text{ g/L}$ ,  $\text{NaNO}_3 = 0.01 \text{ M}$ , Hg light =  $10.5 \text{ MW/cm}^2$ .

**Figure 6.** —Kinetics of thiosulfate removal at pH = 5.3 or 7.4 in a suspension of  $\text{TiO}_2$ .

The presence or absence of oxygen, which is an electron acceptor, also appears to influence the process (Figure 7). Although the initial pH is lower in the test in the absence of  $\text{O}_2$ , it is clear that without an electron acceptor, the oxidation rate is slower. (Note that initial pH increases upon addition of  $\text{S}_2\text{O}_3$  and UV light (sorption); subsequently (during the oxidation process), the pH decreases to 6.5).

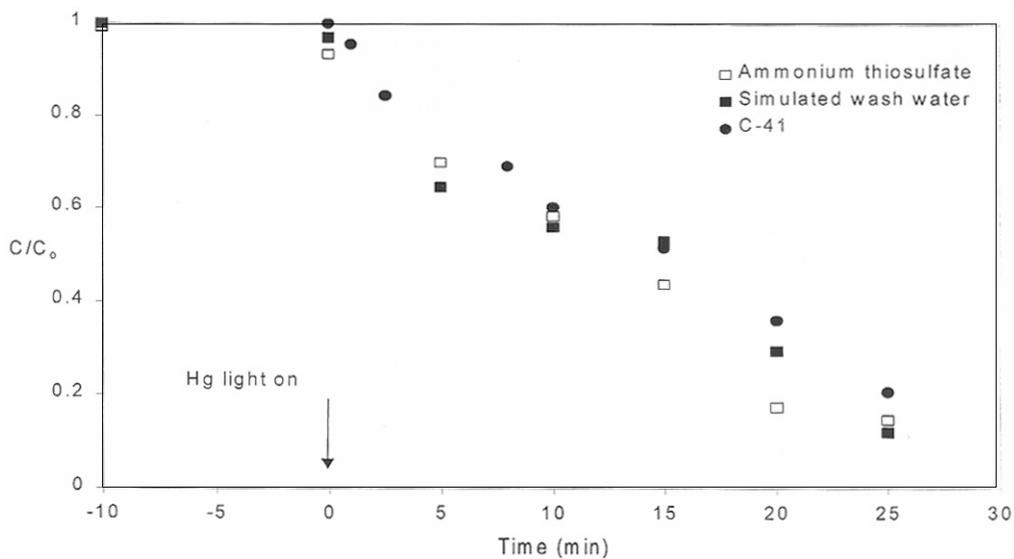
We compared photolytic removal of thiosulfate from test solutions with three different compositions, and observed that there was little effect on the removal rate (Figure 8). In all three cases, about 80 percent of the initial thiosulfate was gone in 25 minutes.

Analogous data for removal of silver (Figure 9) suggest there are some differences among the systems. One difference is that in solutions where silver occurs predominantly as a thiosulfate complex (simulated wash water and C-41), the amount of silver removal via sorption ( $t < 0$ ) is very small. Interestingly, despite the limited initial uptake, subsequent photolytic removal of silver is at least as fast and probably more complete than it is in the silver nitrate solution.



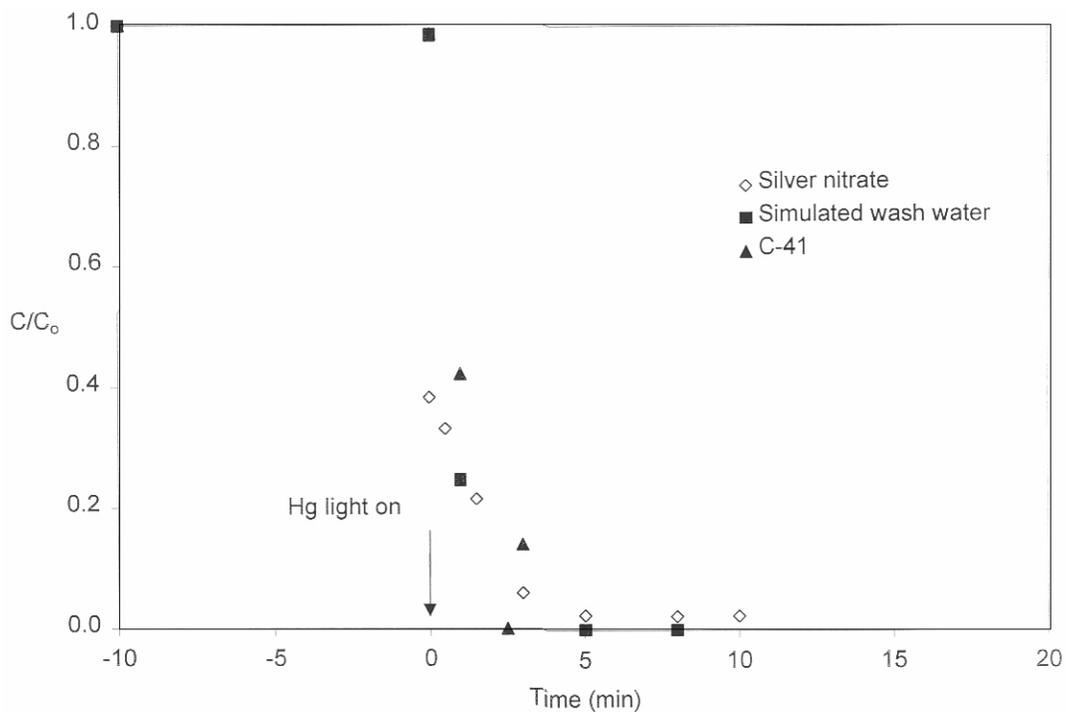
For the test without O<sub>2</sub>, initial pH = 5.35 and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 3.3x10<sup>-3</sup> M;  
 and for the test with O<sub>2</sub>, initial pH = 5.5 and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 2.7x10<sup>-3</sup> M.  
 In both test, TiO<sub>2</sub> = 1.0 g/L, NaNO<sub>3</sub> = 0.01 M, Hg light = 10.5 mW/cm<sup>2</sup>.

**Figure 7.**—Kinetics of thiosulfate removal in a suspension of TiO<sub>2</sub> in the presence or absence of dissolved oxygen.



For (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> total thiosulfate = 10<sup>-3</sup> M and pH = 5.3; for the simulated wash water, S<sub>2</sub>O<sub>3,T</sub> = 10<sup>-3</sup> M and pH = 6.2; for C-41 process, S<sub>2</sub>O<sub>3,T</sub> = 10<sup>-3</sup> M and pH = 5.4.  
 For all systems, TiO<sub>2</sub> = 1.0 g/L Hg light = 10.5 mW/cm<sup>2</sup>.

**Figure 8.**—Kinetics of thiosulfate removal from different test solutions in a suspension of TiO<sub>2</sub>.



For  $\text{AgNO}_3$  total silver = 3.7 mg/L and pH = 5.0; for simulated wash water,  $\text{Ag}_T$  = 3.9 mg/L and initial pH = 6.2; for the C-41 process,  $\text{Ag}_T$  = 8.8 mg/L.

**Figure 9.**—Kinetics of silver removal from different test solutions in a suspension of  $\text{TiO}_2$ .

#### 6-4. PHOTOLYSIS RESULTS SUMMARY

Photolytic removal of silver was rapid in all solutions we tested, whether or not thiosulfate was present. Before the UV light was turned on, there was some initial adsorption of silver. After the UV light was turned on, the silver concentration rapidly dropped, and most of the silver was gone within 10 minutes. The removal rate appears to increase with increasing pH.

Relative to silver, thiosulfate removal was slower and the removal rate decreased with increasing pH. The removal rate increased when oxygen was present in solution. As with silver, thiosulfate could be removed from all the solutions we tested.

### 7. PUTTING THE INITIAL RESULTS IN CONTEXT

Summary results from our initial sorption and photolysis studies must be consistent both internally and in the context of other studies reported in the literature. In the following sections, we examine equilibrium speciation in these systems, surface characteristics of  $\text{TiO}_2$ , and the thermodynamics and likely mechanisms governing redox reactions in these systems.

## 7-1. EQUILIBRIUM SPECIATION IN WASH WATER

Wash water composition is a function of the process specifications and operating procedures at a specific photoprocessing facility. Different types of film have slightly different process specifications; four of the most common processes are ECN-2, ECP-2A, E-6, and C-41. Although the C-41 and E-6 processes are proprietary, fix solution specifications for the ECN-2 and ECP-2A processes are known (Table 3). Following the fix solution, wash water composition varies depending on the wash water flow rate and the efficiency of water removal devices (squeegees). Relative to the fix solutions, wash water typically ends up diluted by about two to three orders of magnitude, resulting in a final total silver concentration ranging from 1 to 10 mg/L.

**Table 3.**—Process specifications for fix solutions for ECN-2 and ECP-2A.

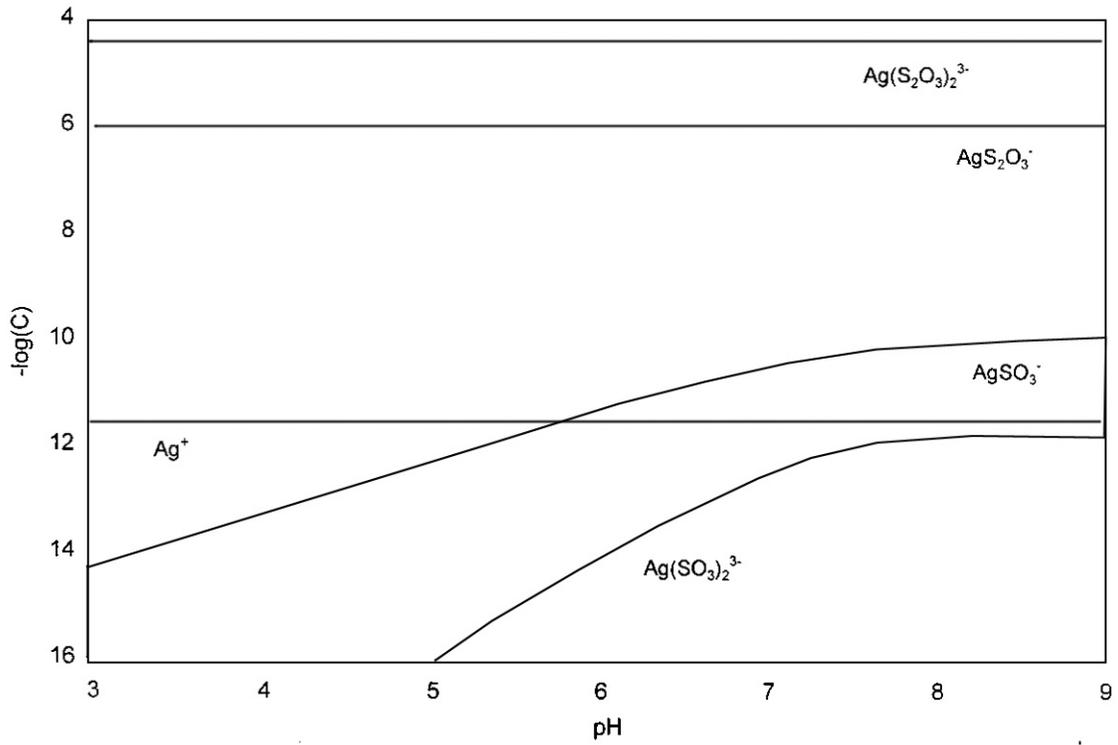
Component	Concentration (g/L) for Process	
	ECN-2	ECP-2A
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	103.7	59.26
Na <sub>2</sub> SO <sub>3</sub>	10	2.5
NaHSO <sub>3</sub>	8.4	10.3

We used these data and the equilibrium program MINTEQA2 (Allison et al., 1991) to examine chemical speciation in these systems. Two new components (H<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>SO<sub>3</sub>) were added to the program, along with appropriate thermodynamic data (acid dissociation constants and silver complex stability constants).

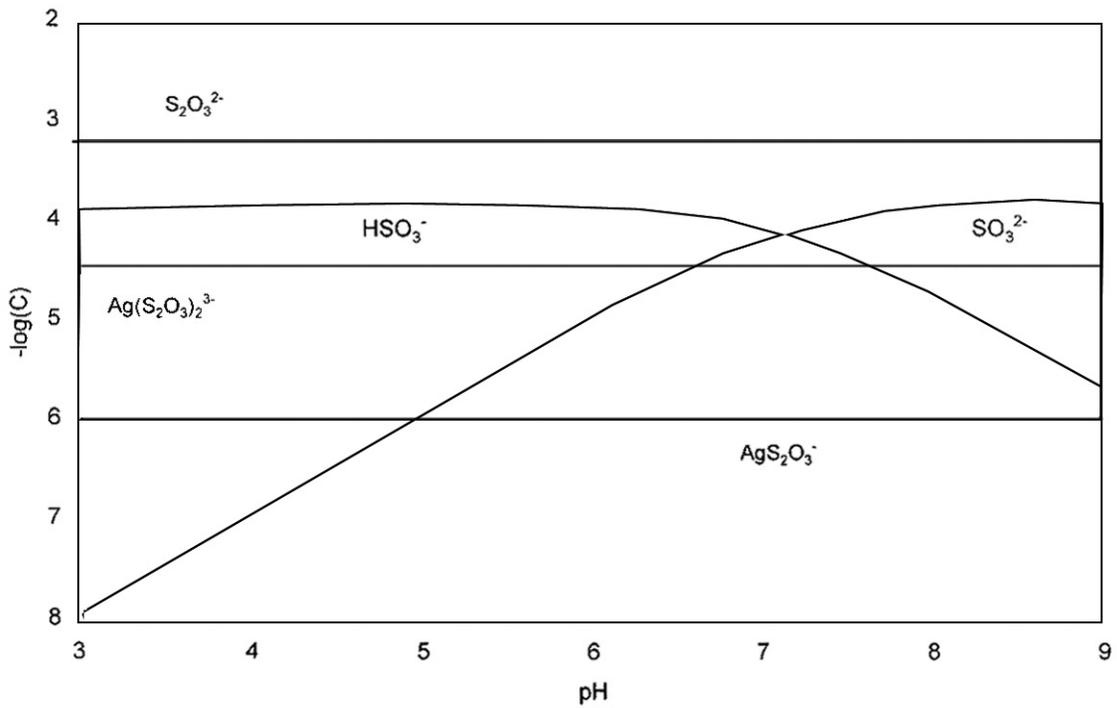
Although photolytic treatment is a dynamic process, this speciation information is useful for describing the initial conditions. In these systems we are mainly interested in speciation of silver and speciation of sulfite and thiosulfate species.

Results for the ECN-2 process are typical. Most of the silver (Figure 10) occurs as Ag(S<sub>2</sub>O<sub>3</sub>)<sup>3-</sup> and most thiosulfate (Figure 11) occurs as S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. Total sulfite, which is used primarily to buffer these solutions, is distributed so that bisulfite (HSO<sub>3</sub><sup>-</sup>) dominates at pH < 7.2 and the sulfite anion (SO<sub>3</sub><sup>2-</sup>) dominates at pH > 7.2 (Figure 11). (Thermodynamic data used to prepare these figures are provided in Appendix A.

Reactions that take place in these solutions depend on the surface characteristics of the TiO<sub>2</sub> catalyst. Effects of these surface characteristics are described in the next section.



**Figure 10.**—Silver speciation vs. pH for ECN-2 process fix solution diluted 1:1000.



**Figure 11.**—Thiosulfate and sulfite speciation vs. pH for ECN-2 process fix solution diluted 1:1000.

## 7-2. PHOTOCATALYTIC REACTIONS WITH TiO<sub>2</sub>

In his comprehensive description of oxidation-reduction reactions at mineral surfaces, Waite (1990) describes photolytic processes at the TiO<sub>2</sub> surface. Much of the information in this section is adapted from that source.

According to band theory, the electronic and optical properties of semiconducting minerals depend on electron energy bands that form in the solid. Electron motion in the solid is restricted by the crystal lattice, so that bands form. There is a valence band that is occupied by electrons, and a conduction band that is unoccupied; the bands are separated by an energy gap. When light of the proper wavelength strikes the solid, energy from the incident light promotes electrons from the valence band to the conduction band. Removal of an electron (e<sup>-</sup>) creates a hole (h<sup>+</sup>) in the valence band. Electrons and holes are the charge carriers that are responsible for conducting electricity. When the band gap of a solid is less than about 5 electron volts (eV), that solid is known as a semiconductor.

Titanium dioxide (TiO<sub>2</sub>) is an n-type, extrinsic semiconductor. The term “extrinsic” refers to the fact that there are defects in the mineral structure, and that these defects are the source of the carriers. The term “n-type” refers to the fact that in TiO<sub>2</sub> electron donor impurities dominate; they donate electrons to the conduction band, and these are the carriers that conduct most of the electricity.

The effective wavelength of the light depends on the energy band gap of the semiconductor. Energy (E) and frequency (ν) of light are related through Plank’s constant (h = 6.626x10<sup>-34</sup> J.s) as follows:

$$\nu = \frac{E}{h}$$

Frequency and wavelength (λ) are related through the speed of light (c = 2.998x10<sup>8</sup> m/s) as follows:

$$\lambda = \frac{c}{\nu}$$

These expressions can be combined to determine the relationship between the band gap energy of the solid and the wavelength of the incident light.

$$\lambda = \frac{c \times h}{E}$$

For TiO<sub>2</sub> the band gap energy ranges from 3.0 to 3.3 eV; the equivalent wavelength of incident light is from 376 nm to 413 nm. Visible light ranges from 400 nm to 700 nm, so shorter wavelength visible light can activate the TiO<sub>2</sub> surface. Most of the useful energy, however, is in the UV (ultra violet) range (< 400 nm).

Once an electron-hole pair is formed, it can simply recombine and release heat. Alternatively, these components can also migrate to the surface of the solid where electrons and holes can respectively reduce and oxidize adsorbed species. Based on the wash water composition, likely oxidation and reduction reactions are discussed in the following section.

### 7-3. POSSIBLE REDOX REACTIONS

Two important factors in determining what reactions take place in these systems are thermodynamics and reaction mechanisms (kinetics). Thermodynamic data can be used to decide what reactions are not possible. Some of the remaining possible reactions might not be feasible, based on considerations of reaction mechanisms.

#### 7-3-1. REACTION THERMODYNAMICS

In theory, a species in these systems can be oxidized if its potential is less than the valence band potential ( $\approx 2.7$  v), and a species can be reduced if its potential is greater than the conduction band potential ( $\approx -0.5$  v). Standard reduction potentials for likely half-cell reactions are summarized in Table 4. Two caveats should be kept in mind when reviewing the table. One is that except for the TiO<sub>2</sub> band potentials, all of the reduction potentials refer to reactions taking place in solution.

**Table 4.**—Standard reduction potentials for reactions that are likely to occur in TiO<sub>2</sub>-photocatalytic treatment of photoprocessing wash waters. (several sources)

Half-Cell Reaction	E° (V)
TiO <sub>2</sub> valence band potential	2.7
O <sub>2(aq)</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> = 2H <sub>2</sub> O	1.27
NO <sub>3</sub> <sup>-</sup> + 6H <sup>+</sup> + 5e <sup>-</sup> = 0.5N <sub>2(g)</sub> + 3H <sub>2</sub> O	1.25
NO <sub>3</sub> <sup>-</sup> + 10H <sup>+</sup> + 8e <sup>-</sup> = NH <sub>4</sub> <sup>+</sup> + 3H <sub>2</sub> O	0.88
Ag <sup>+</sup> + e <sup>-</sup> = Ag <sup>0</sup>	0.80
2SO <sub>4</sub> <sup>2-</sup> + 10H <sup>+</sup> + 8e <sup>-</sup> = S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> + 3H <sub>2</sub> O	0.28
SO <sub>4</sub> <sup>2-</sup> + 3H <sup>+</sup> + 2e <sup>-</sup> = HSO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> O	0.12
SO <sub>4</sub> <sup>2-</sup> + 2H <sup>+</sup> + 2e <sup>-</sup> = SO <sub>3</sub> <sup>2-</sup> + H <sub>2</sub> O	0.10
Ag(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> <sup>3-</sup> + e <sup>-</sup> = Ag <sup>0</sup> + 2S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	0.00
TiO <sub>2</sub> conduction band potential	-0.5

There is little information as to what the potentials are for adsorbed species. The other caveat is that even though thermodynamic data suggest a reaction is possible, it might be inhibited because of the reaction mechanism.

### 7-3-2. REACTION MECHANISMS

One hint of the need to consider reaction mechanisms comes from the work of Prairie et al. (1993). Based on their tests with various metals, they concluded that only metals with half-cell reduction potential greater than 0.3 v could be reduced by TiO<sub>2</sub>. In experiments conducted at pH = 6, where the conduction band potential of TiO<sub>2</sub> is about -0.5 v, concomitant oxidation of salicylic acid was only significant when a metal with a reduction potential of about +0.3 v was involved. They concluded that an overpotential of about 0.8 v was needed.

A second issue to consider is that except for the silver reduction reaction, all reactions in Table 4 involve the transfer of more than one electron. However, most abiotic redox reactions are actually a series of reactions, each involving a one-electron transfer (Stumm and Morgan, 1996). This concept seems especially appropriate for heterogeneous photolytic processes, where a surface reaction site could be defined in terms of an electron or hole that migrates to the surface.

For example, when photocatalytic processes take place in aqueous systems, the reduction of oxygen to water (or the oxidation of water to oxygen) is a potentially important reaction. The overall reaction involves the transfer of four electrons (Table 4). This reaction, however, can be broken down into a series of four sequential reactions, each involving a one-electron transfer. In each of the first three one-electron transfer half-cell reactions, the products (reduced species in Table 5) are reactive, relatively unstable species. From a thermodynamic perspective, the hydroxyl radical (last reaction in Table 5) is the strongest oxidizing agent in this series (it has the greatest potential). In fact, many studies suggest that the hydroxyl radical is the most important oxidizing agent in TiO<sub>2</sub>-based photocatalysis (Turchi and Ollis, 1990; Waite, 1990).

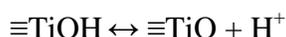
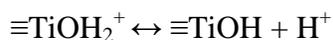
**Table 5.**— Individual one-electron half-cell reactions for the reduction of oxygen to water (Stumm and Morgan, 1996).

Reaction	Reduced Species	E° (v)
$O_{2(aq)} + e^- = O_2^{\bullet - (aq)}$	superoxide radical	-0.16
$O_2^{\bullet - (aq)} + e^- + 2H^+ = H_2O_{2(aq)}$	hydrogen peroxide	1.72
$H_2O_{2(aq)} + e^- + H^+ = OH^{\bullet (aq)} + H_2O$	hydroxyl radical	0.99
$OH^{\bullet (aq)} + e^- + H^+ = H_2O$	water	2.53

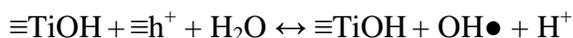
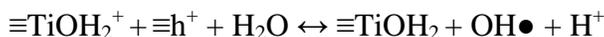
Hydroxyl radicals may play such an important role in photocatalysis because they can be produced through either of two pathways. If oxygen is present in solution and if it serves as an electron acceptor, a hydroxyl radical is the product of the third, sequential, one-electron transfer reaction (Table 5). Alternatively, that same one-electron transfer reaction can be used to describe the oxidation of water (the reverse of the fourth reaction in the table). In the present

context, it might be clearer to think of this alternative as water reacting with a hole at the TiO<sub>2</sub> surface to form a hydroxyl radical.

In water, the surface of an oxide such as TiO<sub>2</sub> is covered with hydroxyl groups. These surface groups (distinguished from bulk solution by the symbol /) participate in proton exchange reactions that can be represented as:



Vohra and Davis (1997) reviewed data from a number of studies of TiO<sub>2</sub> and reported that estimates of the surface site density ranged from 2 to 4 sites/nm<sup>2</sup>. Therefore, there are a significant number of surface sites that, in theory, can participate in redox reactions. Turchi and Ollis (1990) describe such reactions as “hole trapping” reactions that keep the hole from recombining with the electron. These reactions with surface hydroxyl groups can be written as:



The first reaction is more likely below the zero point of charge (ZPC for TiO<sub>2</sub> occurs at 5.6 < pH < 6.5); the second reaction is more likely above the ZPC. Note that we write these reactions emphasizing that the surface hydroxyl group is oxidized by the hole generated within the catalyst. Furthermore, we believe that the hydroxyl radical has little affinity for the TiO<sub>2</sub> surface and, it is released to solution. The surface hydroxyl group is rapidly replaced through reaction with a water molecule.

Finally, it is important to recognize that oxidation-reduction reactions happen in pairs. There is no accumulation of electrons or holes, and the reaction rate is limited by the rate of the slowest reaction. Furthermore, as noted by Waite (1990), electrons are the dominant charge carriers in TiO<sub>2</sub>. Therefore, oxidation reactions involving holes should limit the overall rate of reaction.

## 8. PROCESS SUMMARY: PUTTING IT ALL TOGETHER

When light at a wavelength around 400 nm strikes the TiO<sub>2</sub> surface, electron/hole pairs are generated within the solid. Although the electron and hole can recombine to release heat, they can also migrate to the TiO<sub>2</sub> surface and participate in reduction and oxidation reactions, most likely with adsorbed species.

Oxidation reactions are initiated when holes interact with abundant surface hydroxyl groups to form hydroxyl radicals. These hydroxyl radicals are, in turn, released to solution where they can

oxidize other reduced species. Hydroxyl radicals play an important role in the overall process, because they are powerful oxidizing agents. In solution, they can readily oxidize thiosulfate to sulfate. In the absence of thiosulfate (or other reduced compounds), two hydroxyl radicals can react with each other to form peroxide, which can be oxidized by another hydroxyl radical to form superoxide radical, which can be oxidized by yet another hydroxyl radical to ultimately form oxygen.

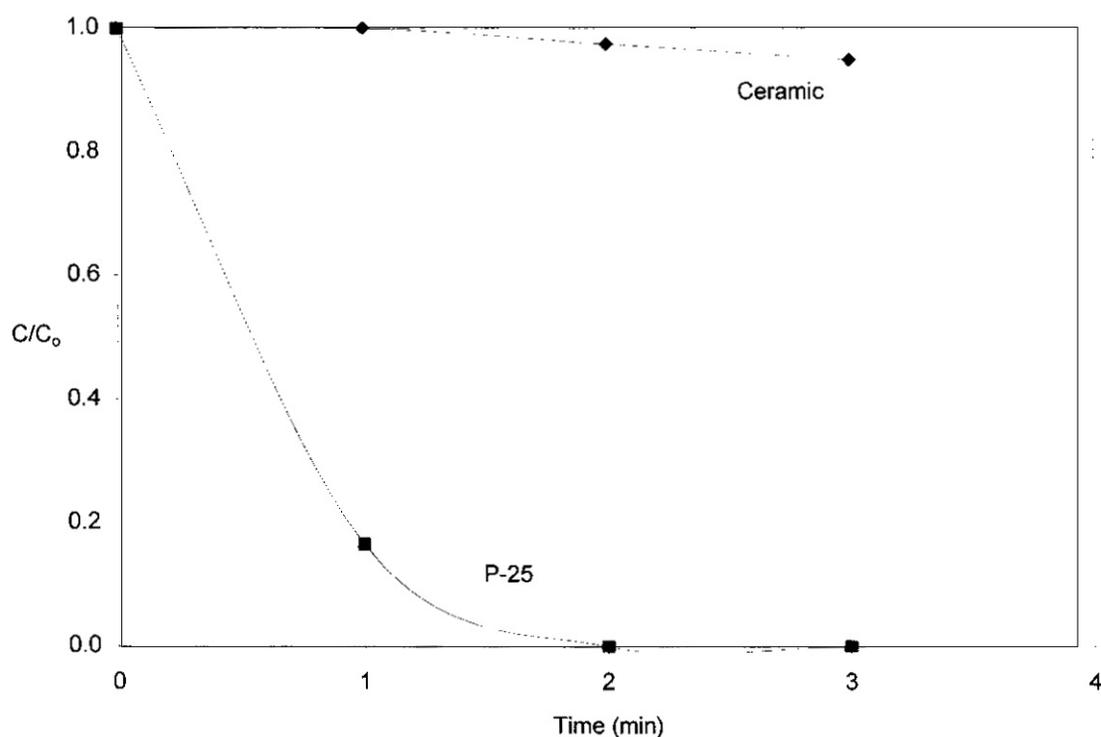
Reduction reactions are initiated when surface electrons react with adsorbed species. In our studies, the most likely reaction is the reduction of ionic silver to elemental silver. In the absence of silver, dissolved oxygen is the most likely electron acceptor. Because it seems unlikely that free electrons travel far from the surface, we believe the dissolved oxygen adsorbs to  $\text{TiO}_2$ .

With this description of the reaction stoichiometry and mechanisms, another objective of this study was to apply this information to develop new catalysts for the treatment of photoprocessing wash waters. Specific goals included trying to maintain the performance of the P-25 catalyst, while developing a catalyst that could be used in a fixed-bed or column process.

## 9. CUSTOMIZING THE CATALYST

Our initial efforts in catalyst synthesis focused on the ceramic material described by Kokubu and Yamane (1985). Although this material could be prepared with a particle size appropriate for a column process, relative to the P-25 catalyst, its photocatalytic properties were disappointing (Figure 12).

Because silver removal using the ceramic catalyst was much worse relative to P-25, we examined a sol-gel fabrication process for synthesizing catalysts. Using the sol-gel process we hoped to prepare binary oxide catalysts that would accomplish several goals. One goal was to increase the catalyst surface area. Because sorption is an important part of the overall process, we hoped that by increasing the surface area of the catalyst, we would increase adsorption onto the surface and increase the reaction rate. A second goal was to increase the pH of the zero point of charge (ZPC) of the catalyst. Here again, because sorption is important, we hoped that a higher ZPC would enhance anion attraction (specific adsorption of the silver cation would not be affected) to the surface and increase the reaction rate. The secondary oxides we used and their approximate ZPCs were  $\text{Fe}_2\text{O}_3$  (ZPC  $\approx$  8.0),  $\text{Al}_2\text{O}_3$  ( $\approx$  9.0), and  $\text{MgO}$  ( $\approx$  12.5). Finally, we also hoped to prepare a catalyst that could be used in a column or fixed-bed process, thereby overcoming the problems associated with removal of colloidal P-25.



Total silver = 4 mg/L,  $\text{NaNO}_3 = 0.01 \text{ M}$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_3 = 1.2 \times 10^{-5} \text{ M}$ ,  $\text{Na}_2\text{SO}_3 = 2.6 \times 10^{-4} \text{ M}$ .

**Figure 12.**— Relative silver concentration vs. time in a suspension of P-25.

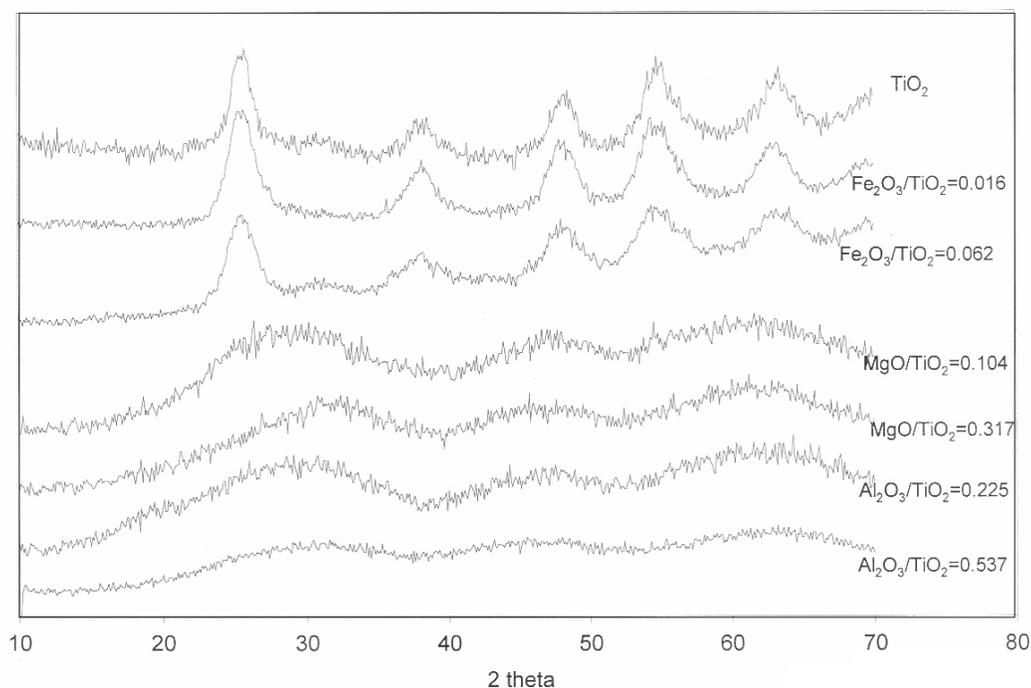
## 10. SOL-GEL CATALYST SYNTHESIS

The composition, surface area, and zero point of charge of the sol-gel catalysts are summarized in Table 6 with similar characteristics of Degussa P-25 included for reference. All of the binary oxides had surface areas greater than the  $\text{TiO}_2$ -only solids. In general, surface area increased and long-range structure decreased (Figure 13) as the mole fraction of the other oxide component was increased. As expected, the pH of the zero point of charge also increased with increasing amounts of the secondary oxides. We were unable to measure the pH of ZPC for the  $\text{MgO-TiO}_2$  solid because it was a relatively soluble compound.

**Table 6.**—Characteristics of Degussa P-25 and a series of catalysts prepared using a sol-gel technique.

Oxide Catalyst	Molar Ratio (oxide/TiO <sub>2</sub> )	BET area (m <sup>2</sup> /g)	pH of ZPC
Degussa P-25	1.0	55	5.2
TiO <sub>2</sub>	1.0	84	5.0
Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	0.225	107	7.4
Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	0.537	196	9.4
Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	0.016	171	7.3
Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	0.062	108	7.8
MgO-TiO <sub>2</sub>	0.104	402	NA
MgO-TiO <sub>2</sub>	0.317	346	NA

X-ray diffraction patterns for the synthesized catalysts (Figure 13) show how the anatase-like structure increases as the amount of the binary oxide component decreases. Catalysts containing Al or Mg appear to be x-ray amorphous; the catalysts containing Fe (which are at least 95 percent TiO<sub>2</sub>) have the characteristic peaks associated with anatase. X-ray peaks for anatase reported at 2-theta = 26, 38, 48, and 55 (Anderson and Bard, 1995; Wei et al.).

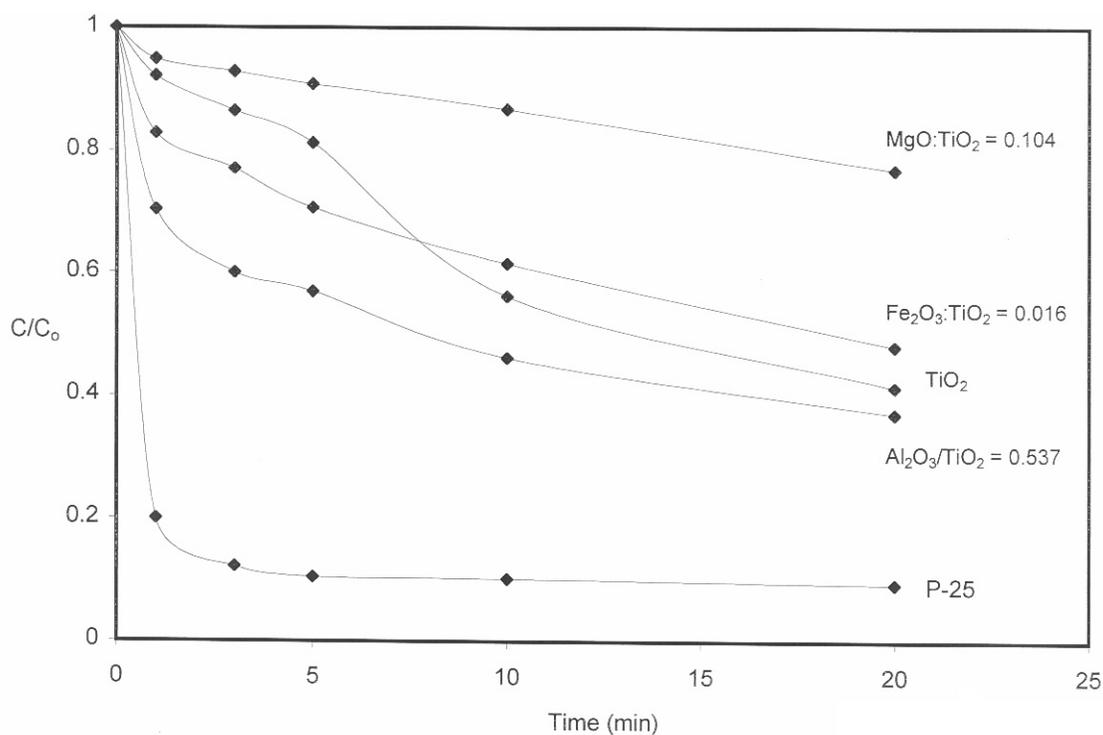


Labels show estimated molar ratios for the components. These patterns have been scaled for display.

**Figure 13.**—Diffraction patterns for catalysts produced using the sol-gel process.

## 10-1. PHOTOCATALYTIC REDUCTION OF SILVER

We conducted a series of tests using a simulated wash water where, as noted above, the vast majority of the silver was complexed as  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ . Representative results from tests with several of these catalysts (Figure 14) indicate that all of the synthesized catalysts suffer in comparison to Degussa P-25. Nevertheless, the  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  catalyst had the best performance of the sol-gel materials. The fact that this solid had the highest surface area and highest ZPC suggests that our hypotheses could be right and that sol-gel synthesis holds promise for catalyst development for treatment of photoprocessing wash waters.



Total silver = 4 mg/L,  $\text{NaNO}_3 = 0.01 \text{ M}$ ,  $\text{Na}_2\text{S}_2\text{O}_3 = 2.6 \times 10^{-4} \text{ M}$ , and solid = 1g/L.

**Figure 14.** —Relative total silver concentration in suspensions of several different catalysts.

## 11. SUMMARY COMMENTS

Echoing the material presented in the above on “Conclusions and Recommendations”, we believe our study demonstrates that a TiO<sub>2</sub>-based photocatalytic process can be an effective wash water treatment process.

- Both free and complexed silver can be reduced.
- Both free and complexed thiosulfate can be oxidized.
- A sol-gel synthesis process can be used to alter the surface charge and surface area of the catalyst, and it shows promise for producing more effective catalysts.

We plan to continue this work by optimizing the catalyst and developing a pilot reactor to use with a variety of wash waters from various photoprocessing facilities.

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## **APPENDIX A**

### **CHEMICAL SPECIATION FOR PHOTOPROCESSING WASH WATERS**

Cumulative formation constants for Ag complexes (Dean, 1992).

Ligand	log K1	log K2
$S_2O_3^{2-}$	8.82	13.46
$SO_3^{2-}$	5.3	7.35
$NH_3$	3.24	7.05

Acid dissociation constants for photoprocessing components (Dean, 1992).

Acid	pK1	pK2
$H_2S_2O_3$	0.6	1.74
$H_2SO_3$	1.89	7.205
$NH_4^+$	9.25	-

Component concentrations and predicted equilibrium pH for dilute (1:1000) ECN-2 and ECP-2A fix process and for the mock wash water used in these tests. These data were developed by adding the thermodynamic data above to MINTEQA2.

Component molar concentrations for process wash waters			
Component	ECN-2	ECP-2A	Mock Wash Water
Ag	$3.71H10^{-5}$	$3.71H10^{-5}$	$3.71H10^{-5}$
$NO_3^-$	$3.71H10^{-5}$	$3.71H10^{-5}$	$3.71H10^{-5}$
$NH_4^+$	$1.40H10^{-3}$	$8.0H10^{-4}$	$1.2H10^{-4}$
$S_2O_3^{2-}$	$7.0H10^{-4}$	$4.0H10^{-4}$	$6.0H10^{-5}$
$SO_3^{2-}$	$1.6H10^{-4}$	$1.19H10^{-4}$	$1.27H10^{-4}$
$Na^+$	$2.39H10^{-4}$	$1.39H10^{-4}$	$2.54H10^{-4}$
$H^+$	$8.07H10^{-5}$	$9.90H10^{-5}$	0
Equilibrium pH	7.04	6.43	8.19

## **APPENDIX B**

### **DATA RECORD**

**Table 1.—Data for Figure 1.**

	Ag(T) mg/L				Ag(T) mg/L	
pH	Dark B 1	Dark - 2		pH	Room light B 1	Room light - 2
2.94	1.6	0.2		4.65	1.64	0.2
2.99	1.62	0.2		4.74	1.38	0.3
3.64	1.4	0.3		6.86	1.06	0.5
4.38	1.49	0.3		6.74	1.14	0.4
5.05	1.3	0.4		7.12	0.97	0.5
7.23	0.85	0.6				
7.32	0.65	0.7				
9.24	0.41	0.8				

**Table 2.—Data for Figure 2.**

Thiosulfate in room light			Thiosulfate in dark		
pH	C (mM)	C/Co	pH	C (mM)	C/Co
4.92	0.005833	0.941667	4.04	0.093333	0.066674
5.24	0.0175	0.825001	4.42	0.093333	0.066674
5.36	0.011667	0.883334	4.72	0.087499	0.125007
5.56	0.011667	0.883334	4.92	0.093333	0.066674
6.07	0.0525	0.475004	5.8	0.081666	0.18334
6.46	0.046666	0.533337	6.06	0.087499	0.125007
6.6	0.064166	0.358339			
6.79	0.064166	0.358339			
7.35	0.075833	0.241673			

**Table 3.—Data from Figure 3.**

pH	Ag (mg/L)	Fraction removed
3.72	0.03	0.997222
3.78	0.07	0.993519
3.99	0.23	0.978704
4.25	0.02	0.998148
4.75	0.02	0.998148
6.63	0.02	0.998148
7.29	0.05	0.99537
7.8	2.59	0.760185

**Table 4.—Data from Figure 4.**

pH	S <sub>2</sub> O <sub>3</sub> (mg/L)	Fraction removed
3.72	0.9	0.9
3.78	0.9	0.9
3.99	0.9	0.9
4.25	15.6	0.1
4.75	1.7	0.9
6.63	1.7	0.9
7.29	2.6	0.8
7.8	3.5	0.8

**Table 5.—Data from Figure 5.**

pH = 5		mg/L		C/Co		pH = 7		mg/L		C/Co	
Time (min)	Rep. 1	Rep. 1	Rep. 1	Rep. 2		Time (min)	Rep. 1	Rep. 1	Rep. 1	Rep. 2	
-10	3.68	3.8	1	1		-10	5.32	6.1	1	1	
0	1.28	1.59	0.347826	0.418421		0	1.07	1.47	0.201128	0.240984	
0.5	1.13	1.35	0.307065	0.355263		0.5	0.45	0.85	0.084586	0.139344	
1.5	0.71	0.9	0.192935	0.236842		1.5	0.07	0.26	0.013158	0.042623	
3	0.18	0.26	0.048913	0.068421		2.5		0.05		0.008197	
5	0.06	0.13	0.016304	0.034211		3	0.07	0.08	0.013158	0.013115	
8	0.06	0.11	0.016304	0.028947		4.5		0.04		0.006557	
10	0.04	0.14	0.01087	0.036842		5	0.04		0.007519		
14	0.03		0.008152			8	0.05		0.009398		

**Table 6.—Data from Figure 6.**

<b>pH = 5.3</b>	<b>C (mM)</b>		<b>C/Co</b>	
Time	Rep. 1	Rep. 2	Rep. 1	Rep. 2
-10	0.991658	0.991658	0.991658	0.991658
0	0.933326	0.933326	0.933326	0.933326
5	0.641661	0.758327	0.641661	0.758327
10	0.583328	0.583328	0.583328	0.583328
15	0.466663	0.40833	0.466663	0.40833
20	0.174999		0.174999	
25	0.116666	0.174999	0.116666	0.174999
<b>pH = 7.4</b>	<b>C (mM)</b>		<b>C/Co</b>	
-10	0.991658	0.991658	0.991658	0.991658
0	0.933326	0.933326	0.933326	0.933326
5	0.874993	0.874993	0.874993	0.874993
10	0.874993	0.874993	0.874993	0.874993
15	0.758327	0.758327	0.758327	0.758327
20	0.699994	0.758327	0.699994	0.758327
25	0.641661	0.758327	0.641661	0.758327
30	0.641661	0.699994	0.641661	0.699994

**Table 7.—Data from Figure 7.**

<b>pH(i) = 5.35</b>	<b>No O<sub>2</sub></b>		<b>pH(i) = 5.5</b>	<b>O<sub>2</sub></b>
<b>Time (min)</b>	<b>C/C(0)</b>		<b>Time (min)</b>	<b>C/C(0)</b>
-10	1.00		-10	1.00
6	0.71		0	0.95
16	0.69		15	0.83
25	0.65		25	0.79
40	0.64		31	0.74
60	0.64		41	0.65
75	0.63		65	0.53
			81	0.37

**Table 8.**—Data from Figure 8.

Time	C/Co		
	C-41	Simulated	Ammonium thiosulfate
-10	1	1	0.991658
0	1	0.970588	0.933326
1	0.955	NA	NA
2.5	0.845	NA	NA
5	0.647	0.647059	0.699994
8	0.691	NA	NA
10	0.603	0.558824	0.583328
15	0.515	0.529412	0.437496
20	0.361	0.294118	0.174999
25	0.207	0.12	0.145832

**Table 9.**—Data from Figure 9.

Time (min)	C/Co		
	Silver nitrate	C-41	Simulated
-10	1	1	1
0	0.383124	0.984659	0.98326
0.5	0.331164		
		0.421591	0.246114
1.5	0.214888		
		0	
3	0.058667	0.139205	
5	0.025257		0
8	0.022626		0
10	0.023856		

**Table 10.—Data from Figure 10.**

pH	-log(C)				
	Ag+	AgS2O3-	Ag(S2O3)2-3	AgSO3-	Ag(SO3)23-
3	11.46	5.96	4.44	14.22	20.02
3.5	11.49	5.97	4.44	13.72	19.01
4	11.49	5.97	4.44	13.22	18.01
4.5	11.50	5.97	4.44	12.72	17.01
5	11.50	5.97	4.44	12.22	16.02
5.5	11.50	5.97	4.44	11.73	15.03
6	11.50	5.97	4.44	11.25	14.07
6.5	11.50	5.97	4.44	10.81	13.19
7	11.50	5.97	4.44	10.46	12.49
7.5	11.50	5.97	4.44	10.24	12.05
8	11.50	5.97	4.44	10.15	11.85
8.5	11.50	5.97	4.44	10.11	11.77
9	11.50	5.97	4.44	10.09	11.75

**Table 11.—Data from Figure 11.**

pH	-log (C)					
	AGS2O3-1	Ag(S2O3)23-	AgSO3-	S2O32-	HSO3-	SO32-
3	5.962573502	4.443697499	14.21538271	3.222573178	3.826813732	7.954677021
3.5	5.970616222	4.443697499	13.71896663	3.209011525	3.806875402	7.438898616
4	5.970616222	4.443697499	13.22112553	3.20481541	3.798602876	6.935542011
4.5	5.974694135	4.443697499	12.7235382	3.203425667	3.798602876	6.432973634
5	5.974694135	4.443697499	12.22475374	3.202732459	3.798602876	5.935542011
5.5	5.974694135	4.443697499	11.73282827	3.202732459	3.806875402	5.441291429
6	5.974694135	4.443697499	11.25258819	3.202732459	3.826813732	4.962573502
6.5	5.974694135	4.443697499	10.81247928	3.202732459	3.886056648	4.521433504
7	5.974694135	4.443697499	10.4609239	3.202732459	4.035269079	4.168770306
7.5	5.974694135	4.443697499	10.24488773	3.202732459	4.317854924	3.950781977
8	5.974694135	4.443697499	10.14508698	3.202732459	4.718966633	3.850780887
8.5	5.974694135	4.443697499	10.10734897	3.202732459	5.180456064	3.815308569
9	5.974694135	4.443697499	10.09258864	3.202732459	5.665546249	3.801342913

**Table 12.—Data from Figure 12.**

	Ceramic		P-25	
Time (min)	mg/L	C/Co	mg/L	C/Co
0	3.9	1	3.911	1
1	3.9	1	0.647	0.165431
2	3.8	0.974359	0	0
3	3.7	0.948718	0	0

**Table 13.—Data from Figure 13.**

Time, min	Degussa	Ti10/Al5	Ti5/Al10	Ti10/Fe5	Ti5/Fe10
0	3.967	3.969	3.969	3.85	3.925
1	0.794	2.182	1.697	3.191	3.387
3	0.484	2.162	1.058	2.968	3.069
5	0.415	1.9	0.688	2.719	2.934
10	0.404	1.427	0.332	2.368	2.59
20	0.368	0.883	0.181	1.849	2.285

**Table 14.—Data from Figure 14.**

Time, min	Ti10/Mg5	Ti5/Mg10	Ti15	Ti10/Al5	Ti5/Al10
0	3.986	3.986	2.926	3.918	3.918
1	3.782	3.775	2.697	3.056	2.756
3	3.702	3.671	2.532	2.659	2.352
5	3.623	3.689	2.379	2.44	2.231
10	3.461	3.765	1.644	2.102	1.808
20	3.066	3.683	1.209	1.707	1.448